

CARBON DIOXIDE THICKENING AGENTS FOR REDUCED CO₂ MOBILITY

by

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ABSTRACT

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The objective of this work is to design, synthesize, and evaluate direct carbon dioxide thickeners. The thickener must dissolve in CO₂ without the introduction of a cosolvent. The thickener, in dilute solution of less than one weight percent, should be capable of at least doubling the viscosity of dense CO₂ at temperature and pressure conditions characteristic of CO₂ EOR floods.

A bulk-polymerized, random copolymer of fluoroacrylate (71mol%) and styrene (29mol%), Mn=540,000, has been identified as an efficient CO₂ thickener using falling cylinder viscometry and flow-through-porous-media viscometry. For example, a 0.5wt% solute of the random copolymer in CO₂ tripled the viscosity of liquid CO₂ flowing through a 100md sandstone core at superficial velocities of 1~10ft/day.

Non-fluorous polymers are also investigated in an attempt to identify a less expensive, more environmentally benign thickener. Our first step is to identify a highly CO₂-philic, hydrocarbon-based polymer. Among all commodity polymers, poly vinyl acetate, PVAc, is identified as the most CO₂ soluble, non-fluorous, hydrocarbon-based commercial available polymer. Nonetheless, PVAc does not exhibit sufficient solubility in CO₂ at reservoir conditions to form the basis of a class of CO₂ thickeners.

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1.0 INTRODUCTION

Oil is an important energy source. All over the world, the demand for petroleum products has continued to rise. In Europe and North America, most of the easily exploitable petroleum reservoirs have already been found and overall production is in decline. Therefore, it is becoming more important to get more oil with enhanced oil recovery from existing fields. Several mechanisms are employed in the recovery of crude oil. Primary production, producing oil under its own pressure and/or by the expansion of the dissolved gas, accounts the recovery of 5-20% of the oil. Secondary production, the injection of water to displace the oil, can recover nearly 50% of the oil. There are several tertiary methods employed after water flooding that may be considered to recover the remaining oil.

1.1 Enhanced Oil Recovery (EOR)

Enhanced or improved oil recovery processes employ fluids other than water to recover oil, and are referred to as tertiary processes if they are employed after water flooding. EOR methods include hydrocarbon miscible flooding, CO₂ flooding, polymer flooding, steam flooding, immiscible gas injection. They inject different fluids to displace additional oil from reservoir, via several mechanisms including: solvent extraction to achieve (or approach) miscibility, interfacial-tension (IFT) reduction, improved sweep efficiency, pressure maintenance, oil swelling, and viscosity reduction.^[1]

Among these EOR methods, gas or vapor flooding dominates the EOR production. More than 75% of the EOR projects in North America involve injection of steam, CO₂, or light hydrocarbon solvents. Due to the expense of hydrocarbon-based solvents, such as LPG, few hydrocarbon miscible floods are currently conducted. Steam flooding is typically applied to heavy, viscous crude oils that require substantial viscosity reduction. Carbon dioxide is typically applied to post-water flooded oil fields that retain significant amount of light oils.^[2] CO₂ flooding has many advantages that have made it a widely employed EOR technique in the southern US. CO₂ is environmentally benign, available in large amount from natural reservoirs, inexpensive, nonflammable, and non-toxic except as an asphyxiant. A large number of field applications have been initiated in the past decade, especially in Texas and New Mexico. Currently, roughly 1.2 billion SCF of CO₂ are injected into domestic reservoirs each day.

The main disadvantage of CO₂ flooding is its low viscosity, which can contribute to low sweep efficiency. In a typical reservoir, temperature is usually between 80 and 250°F, and the pressure will be kept over MMP, minimum miscibility pressure, Figure 1.1^[3] At these conditions, the CO₂ has viscosity around 0.06cp, Figure 1.2. The reservoir oil has viscosity between 0.1 and 50 cp. This viscosity ratio leads to a mobility ratio,

$$M = \frac{K_{CO_2}}{m_{CO_2}} \bigg/ \frac{K_{oil}}{m_{oil}}$$

which is greater than unity, because the permeability of CO₂ and oil are comparable in magnitude. This unfavorable mobility ratio contributes to “miscible viscous fingering”, Figure 1.3. As a result, CO₂ bypasses much of the oil in the reservoir, which reducing the areal sweep efficiency. Low viscosity of CO₂ also contributes to the low vertical sweep efficiency, especially in stratified reservoirs. The highly mobile CO₂ enter the most permeable zones, and the oil

residing in the low permeable zones cannot be efficiently displaced. Although the injection of large volumes of CO₂ will eventually lead to improved sweep efficiency, an increase in CO₂ viscosity would result in an increased rate of oil recovery. Therefore, an increase in the viscosity of CO₂ could substantially increase economics of the oil recovery project. It has been estimated by US DOE National Petroleum Technology Office that if the viscosity of the CO₂ could be increased by a factor of 2-10, the resultant oil production would increase from the current level of 180,000 barrels per day (about 3% of domestic oil production) to 400,000 barrels per day.

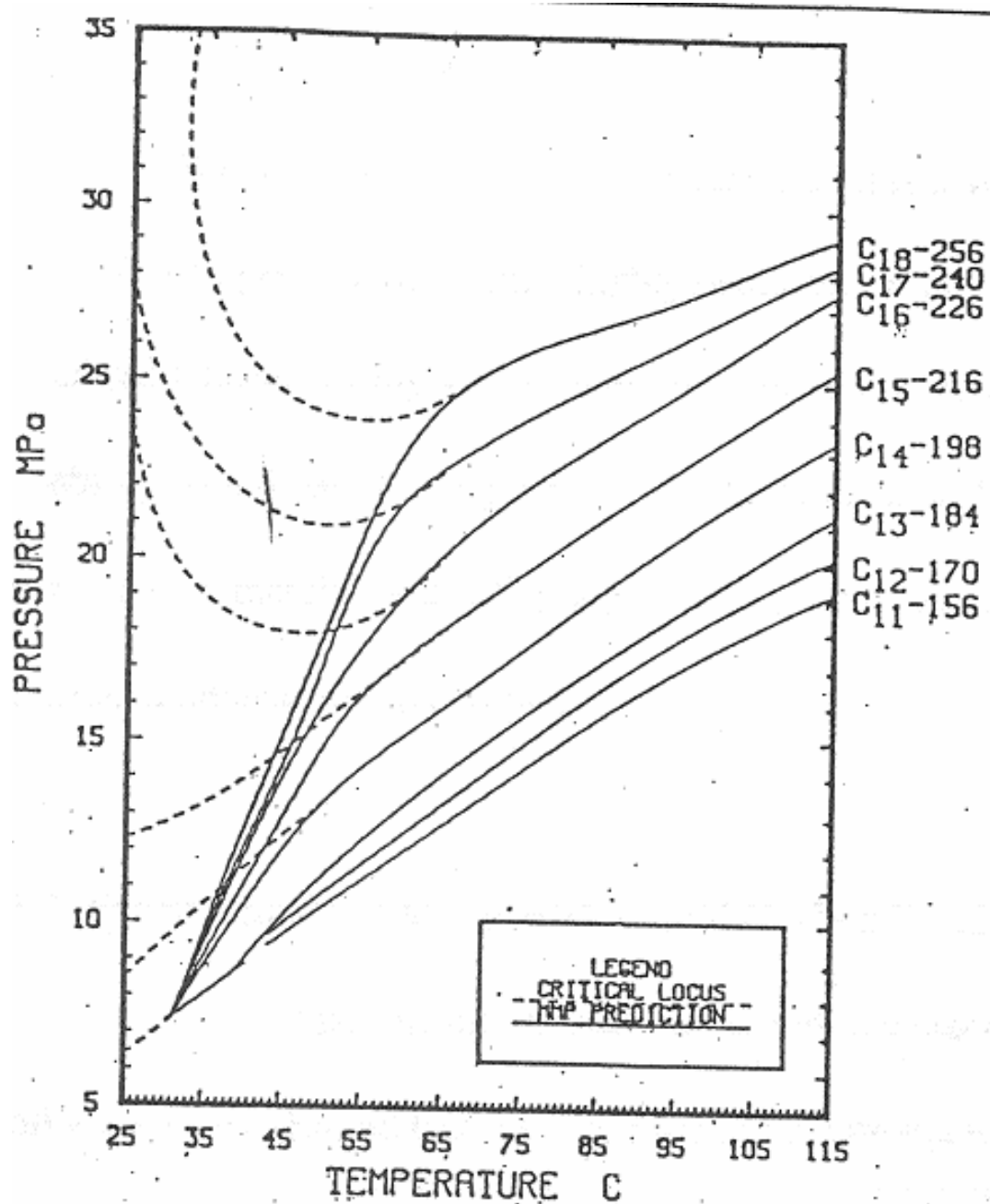


Figure 1.1 Minimum miscibility pressure (MMP) ^[3]

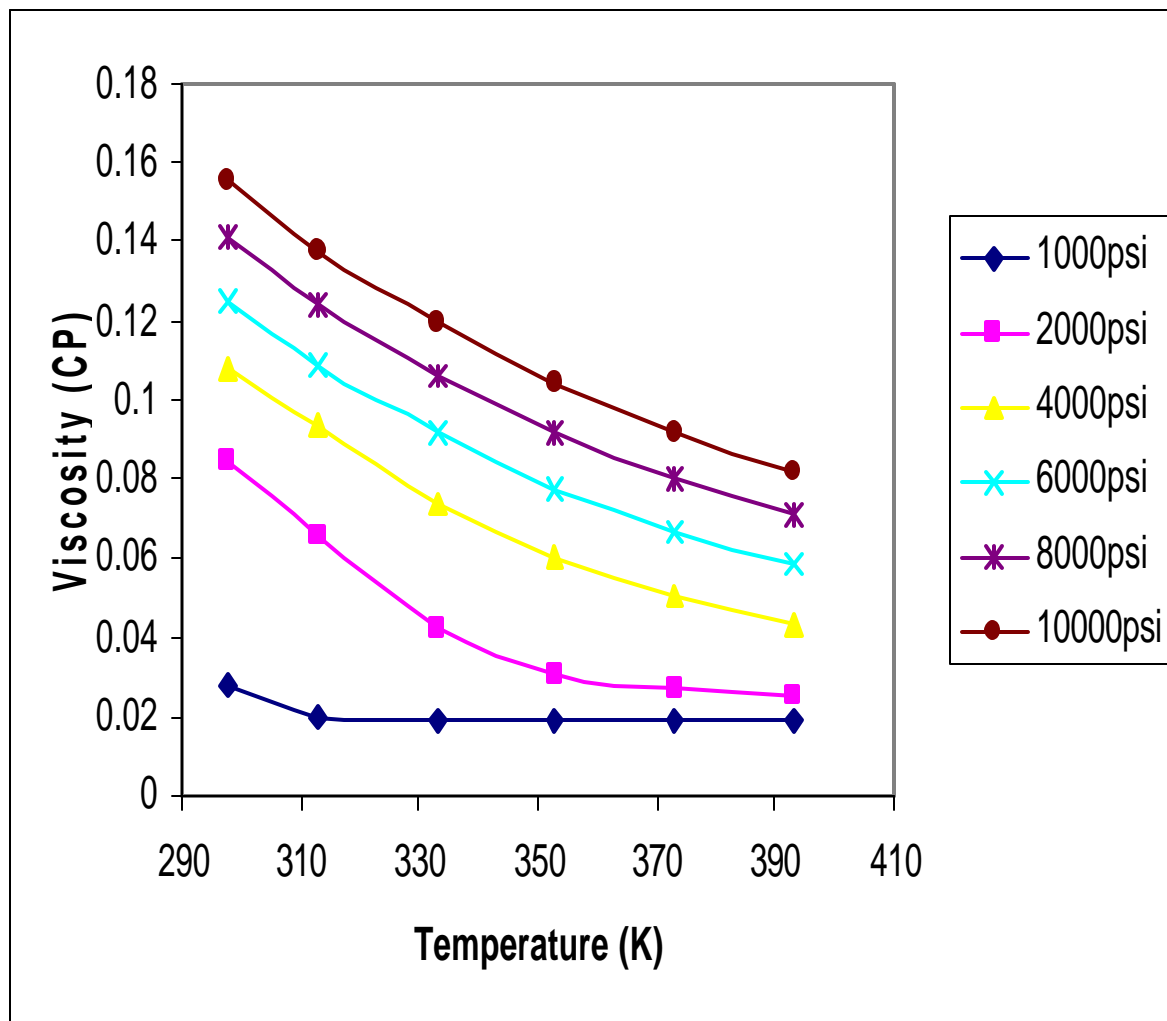


Figure 1.2 Viscosity of carbon dioxide

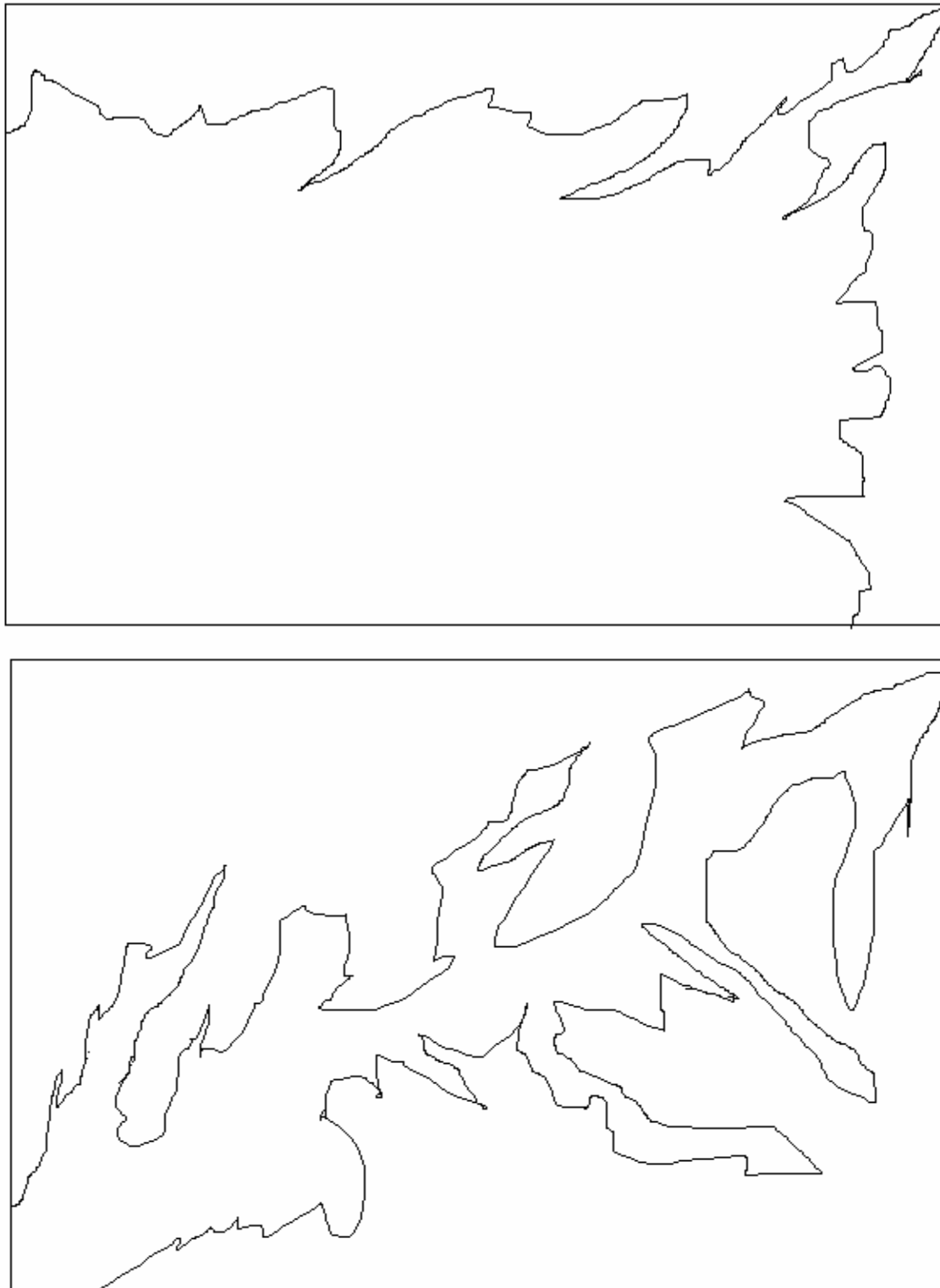


Figure 1.3 Viscous miscible fingering

(a) very slightly unfavorable mobility ratio (b) highly unfavorable mobility ratio

1.2 CO₂ for Formation Fracturing

Besides EOR, liquid CO₂ is also widely used in fracturing formation as a proppant carrier for sand fracturing. In this process, cold CO₂ (-20°C) is delivered to a well site using tanker trucks. Liquid CO₂ is then rapidly injected into the tight gas formation, generating elevated pressures. When this pressure (typically 5000~10000 psia) cause a vertical fracture to form 1/8~1/2” in width, a distinct pressure drop is observed at the wellhead. Sand is then slurried into the CO₂, and pumped into the fracture. Typically, the fracture collapses in less than one minute, and the sand particles that flow into the fracture “prop” it open, providing a high permeability flow path for the gas.

If the viscosity of CO₂ could be increased, the efficiency of this process could be increased in three ways: large proppant could be used, decreased leakoff of CO₂ into the fracture faces could occur, and an increased extent of the fracture would be achieved. The thickener would cause skin damage as it precipitates when the CO₂ is produced from the fracture.

2.0 BACKGROUND AND LITERATURE REVIEW

The high mobility of CO₂ has a significant influence on flooding efficiency. Therefore, much research has been done in order to increase the flooding efficiency. The only commonly employed technique of CO₂ mobility reduction is the water-alternating-gas technique, which lowers CO₂ mobility by reducing relative permeability to CO₂ via increased water saturation. CO₂-foams (high volume fraction CO₂ foams with continuous lamellae of aqueous surfactant solutions) have such low mobility that they are used for profile modification (blocking high permeability, watered-out zones). The mobility of these foams cannot be easily or reliably controlled or moderated to the levels required for mobility control.

2.1 WAG

The use of the water-alternating-gas (WAG) procedure ^[4, 5] decreases the relative permeability of CO₂ by increasing the water saturation within the porous media. The main advantage of this method is that both CO₂ and water are inexpensive and readily available in large volumes. However, this injection of large volumes of water prolongs the duration of the CO₂ flood. Further, there are concerns that the additional water in reservoir may shield residual oil from CO₂ flooding and increase the mass transfer resistance associated with the displacement.

2.2 Previous Attempts to Increase the Viscosity of CO₂

2.2.1 Entrainers (cosolvents)

Llave and coworkers^[6, 7] used entrainers (cosolvents) to improve CO₂ mobility control. The definition of entrainer, based on this approach, is a chemical additive that enhances the viscosity of CO₂ and the solubility of crude oil components in the CO₂-rich phase. The cosolvents included n-decanol, ethoxylated alcohols, isooctane and 2-ethylhexanol. Even though substantial viscosity increases were reached, large amounts of the entrainers were employed. For example, viscosity increases of 243% were attained with isooctane and an increase of 1565% was realized with 2-ethylhexanol. The entrainer concentrations of 13 mole% and 44 mole%, respectively, were very high.

2.2.2 In-situ Polymerization of CO₂ Soluble Monomers

Terry and coworkers^[8] attempted to increase CO₂ viscosity by in-situ polymerization of monomers miscible with CO₂. The polymerization is carried out while the monomer (solute) is in the CO₂ supercritical phase (solvent). The polymerizations were successfully carried out at approximately 160°F and 1800 psi, the temperature and pressure are typical for oil reservoirs in which CO₂ is applied as a miscible fluid. The apparatus used for polymerization also allowed the measurement of the viscosity of the resultant CO₂/polymer system. However, even though the polymers were made successfully, no apparent viscosity increases were detected because the polymers were CO₂-insoluble and precipitated during the reaction.

Lancaster and coworkers also tried in-situ “polymerization”, a reaction between organic titanates with organic substrates, which include pyrogallol, resorcinol, silicic acid, phenol, hydroquinone.^[9,10] A fast reaction did take place between organic substrate and titanate, but the products were completely insoluble in liquid CO₂. Noting the gelation of diesel oil after the interaction of an amine with gaseous CO₂ in diesel, they also hoped the reaction products of liquid CO₂ and mono n-butylamine would be soluble in liquid CO₂. The product was CO₂-insoluble, however.

2.2.3 Small, Associating Compounds

Heller and coworkers considered organometallic compounds as CO₂ viscosifiers.^[11,12] They studied the solubility of organotin fluorides in various solvents including dense CO₂. The trialkyltin fluorides have structure R₃SnF, and associate in the form of a penta co-ordinate species. R represents alkyl, alkylaryl, or aryl group. Because of electronegativity differences between tin and fluorine atoms, there exist dipole moment in these molecules, which cause weak dipole-dipole interactions between adjacent molecules. Even at low concentrations (less than 1wt%), this transient polymer can increase the viscosity of non-polar solvents by several orders of magnitude. Tri-n-butyltin fluoride is a representative example of these organometallic viscosifiers. Although these polymers viscosified liquefied petroleum gas, they did not thicken CO₂ due to their low CO₂ solubility.

The research in University of Pittsburgh began with surfactants, which contain a hydrophilic and hydrophobic functional group. None of 70 commercially available surfactants were soluble in CO₂. Secondly, tributyltin fluoride, a well-known alkane-gelling agent in CO₂

was investigated. Although it was able to increase the CO₂ viscosity by several orders of magnitude in low concentration, very large amounts of pentane cosolvent were required. Polyfluoroether oils were also investigated. They all easily dissolved in liquid CO₂ at relatively low pressures, but no significant viscosity increase was detected, even at concentrations of 5-10 wt%.

Recently, a modified semifluorinated trialkyltin fluoride was evaluated as a direct CO₂ thickener. Carbon dioxide solubility was enhanced by introducing the fluoroalkyl functionality into the trialkyltin fluoride molecular structure. Tris(2-perfluorobutyl ethyl)tin fluoride was highly soluble in liquid CO₂ at moderate pressure. The solution viscosity was raised by only 3.3 times at a concentration of 4wt% with this low molecular weight compound, however. This modest viscosity increase was attributed to strong solute-solvent interactions and/or competition between the fluoroalkyl fluorine and the fluorine bonded to the tin for association with tin of the adjacent molecule.

Fluoroalkyl aspartate bisureas and ureas were synthesized and evaluated as potential CO₂ thickener. All samples were soluble in CO₂ at pressure below 7000psi, and temperature below 100°C. The fluoroether bisureas and ureas were more soluble in CO₂ than fluoroalkyl bisureas and ureas, because the fluoroether functionality was more CO₂-philic than fluoroalkyl functionality. However, of all of ureas which were soluble in CO₂ at room temperature and pressure below 5,000psi, none increased the solution viscosity significantly.

2.2.4 Dissolution of Conventional Polymers into CO₂

A polymeric direct CO₂ thickener must be soluble enough in CO₂ at reservoir conditions that it can induce an increase in viscosity. Ideally, the thickener can increase viscosity 2-10 times in concentration of 1wt% or less.

Heller and coworkers at the NMIMT tested about 40 commercially available polymers. They found only about 30% of these polymers were slightly soluble in dense CO₂. In general, these were also soluble in light hydrocarbons and were completely insoluble in water. These oil-soluble polymers are mostly based on straight-chain hydrocarbons, with low molecular weight, and are atactic in their molecular structure. However, none of these polymers were able to increase the viscosity of the resulting solution, because their MW and/or solubility in CO₂ were too low.

Heller and coworkers then synthesized poly- α -olefins. The method comprised of the synthesis of homo-, co-, and ter-polymers of various α -olefins(1-olefins) in the C5 to C12 range. The goal was to synthesize amorphous and atactic polymers of varying molecular weights and with side chains, which vary in carbon numbers. The aim was to synthesize a polymer with high entropy from irregularity and disorder, which would cause it to be easily dissolved in dense CO₂. They studied the Ziegler-Natta catalysts, the reaction conditions, and the effect on the structure. The results were not promising, as these polymers did not induce a significant viscosity increase due to their low CO₂-solubility.

Heller and coworkers also considered telechelic ionomers. Ionomers are hydrocarbon polymers containing relatively few ionic groups pendent to a hydrocarbon polymer chain. They studied the possibility of using hydrocarbon-based telechelic ionomer as an effective thickener

for dense carbon dioxide in their evaluation of sulfonated polyisobutylene.^[13] Due to its low solubility in dense CO₂, the ionomer did not enhance the viscosity of CO₂ substantially.

Lancaster and coworkers^[9, 10] also tried to increase the liquid CO₂ viscosity via polymer addition. They considered caprolactone polymers including either aliphatic alcohol or methoxy acetic acid terminations, and the others were copolymer condensate products of caprolactone and ethyleneimine. All polymers were insoluble in liquid CO₂, and precipitated out of solution as solids or oils.

Davis, Irani and coworkers^[14-18] found a series of polymers which were useful in increasing the viscosity of carbon dioxide. The polymers included polysilylenesiloxane, polysilalkylenesilane, polyalkylsilsesquioxane and polydialkylsilalkylene polymers. An extensive experimental program identified a number of polymer types that could be dissolved in CO₂ with the addition of cosolvents. They also studied suitable types of polymers and cosolvents^[19] They also investigated the CO₂ flooding process in laboratory, using a sight glass for solubility measurements and a core flood apparatus for mobility measurement. In their core testing, oil recovery tests were also performed. Oil recovery was accelerated and CO₂ breakthrough was delayed with viscosified CO₂. The displacement efficiency was improved over regular CO₂ flooding. The disadvantage of their method is it required a significant amount of cosolvent (e.g. 15% toluene) to dissolve a high molecular weight silicone polymer capable of increasing the viscosity of carbon dioxide.

DeSimone and coworkers^[20, 21] found amorphous (or low melting) fluoropolymers and silicones are soluble in CO₂ at readily accessible conditions (T<100C and P<450bar). These soluble polymeric materials are termed as CO₂-philic. They synthesized poly(1, 1-dihydroperfluorooctyl acrylate)(PFOA), Mw~1.4*10⁶, with free radical synthesis. PFOA was

synthesized in supercritical CO₂, with AIBN initiator. The visual cloud point is 220 bar for 3.7 w/v%. The viscosity result indicated that PFOA significantly increased the CO₂ viscosity. CO₂ solutions with 3.7w/v% and 6.7w/v% PFOA have viscosity 0.25cp and 0.55cp in 360bar, respectively, while the viscosity of neat CO₂ is about 0.1cp. This was the first reported viscosity enhancement of CO₂ without the use of a cosolvent. Although the degree of thickening at dilute concentrations was not as substantial as desired for EOR, this work demonstrated that CO₂ thickeners could be made by designing the thickener specifically for dissolution in CO₂.

Enick and coworkers also evaluated fluorinated telechelic disulfate, by introducing CO₂-philic fluoroether functionality into the structure of polyurethane telechelic disulfate. The compound was highly soluble in liquid CO₂ at pressure lower than 7000psi. There existed an optimal molecular weight of about 19000, where the fluorinated disulfate exhibited the highest solubility in CO₂. Below this molecular weight, the CO₂-philic fluoroether content diminished and the disulfate became more polar and the CO₂-solubility decreased. As the molecular weight increases above 19000, the effect of unfavorable entropy of mixing decreases the solubility in CO₂. The CO₂-phobic disulfate end groups promoted intermolecular association in CO₂ environment more effectively than high molecular weight CO₂-soluble polymers. These relatively low molecular weight ionomers were more effective than high molecular weight random polymers, such as poly(heptadecafluorodecyl acrylate), in solution viscosity increase at comparable weight concentrations. The increases in viscosity were only 2-3 fold at concentration up to 5wt%, were still not significant enough for EOR applications.

Fluorinated aspartate methacrylate urea/ fluoroacrylate copolymers were synthesized and evaluated as potential CO₂ thickener. The concentration and the composition of the copolymer have significant effect on the polymer solubility and solution viscosity. A CO₂-philic

functionality such as fluoroacrylate was necessary to impart CO₂ solubility of the polymer; on the other hand, the content of hydrogen bonding functionality was required in order to increase the solution viscosity. The copolymer with an acryl/urea molar ratio of 19.5 was able to increase solution viscosity by 9 times at 5wt%.

2.3 Solubility of Polymers and Copolymers in Supercritical CO₂

In order to use a polymer or copolymer as a direct thickener for CO₂ viscosity, it must be designed to dissolve in CO₂. Carbon dioxide is a good solvent for a variety of polymer and copolymers. McHugh and coworkers have shown that CO₂ can easily dissolve polymeric oils, such as polydimethylsilicone, polyphenylmethylsilicone, perfluoroalkylpolyethers, and chloro- and bromotrifluoroethylene polymers.^[22, 23] In general, many investigators have confirmed that the most CO₂-philic polymers are fluorinated or silicone-based. Carbon dioxide is a feeble solvent for nearly all other types of hydrocarbon-based polymers. Nonetheless, a significant effort has been made to identify classes of commercial polymers that can dissolve in carbon dioxide.

Heller and coworkers extensively tested many hydrocarbon-based polymers. The polymers they found to be soluble at least in parts-per-thousand range in dense CO₂ at 25°C included poly α -decene, polybutene atactic, polyisobutylene, polyvinylethylether, polymethyloxirane atactic. They also listed the polymers that are insoluble in CO₂.^[11] They found that even the most soluble polymer poly α -decene, its solubility is less than 1wt% at pressure of 2900psi. Even though their initial goal was to find a polymer with viscosity increase ratios of 20~30, the best polymers they found showed values of this parameter of less than 1.3. Although

no viscosity enhancing polymer was identified, hydrocarbon-based polymers that exhibited slight solubility in CO₂ had solubility parameters less than 8 (cal/cm³)^{0.5}. Ghenciu calculated the solubility parameters in his PhD dissertation, and the solubility parameter of liquid CO₂ is found to be in the range of 4 to 5 (cal/cm³)^{0.5} at 298K and pressure above 10MPa.^[24]

McHugh and coworkers investigated the solubility of poly(acrylates) in CO₂ at temperature and pressure up to 270°C and 3000bar, respectively.^[25] The poly(acrylates) includes methyl, ethyl, propyl, butyl, ethylhexyl, octadecyl. They also studied the random copolymer of poly(ethylene-co-methyl acrylate), poly(tetra fluoro ethylene-co-hexa fluoro propylene). They found that CO₂ could not dissolve polyethylene, poly(acrylic acid), poly(methyl methacrylate), poly(ethyl methacrylate), polystyrene, poly(vinyl fluoride), poly(vinylidene fluoride) at their experimental working condition. Polyacrylates were found to exhibit solubility in carbon dioxide, but at pressures an order-of-magnitude or greater than that associated with EOR. For example, the cloud point pressure of poly(methyl acrylate) varied from 2500 bar at 25°C to 1600 bar at 200°C. They also found poly(vinyl acetate) was the most carbon dioxide soluble non-fluorous polymer they detected, even though it has the same chemical formula as poly(methyl acrylate), it was much more carbon dioxide soluble than poly(methyl acrylate).

Beckman and coworkers found non-fluorous polymers with very high solubility in supercritical CO₂.^[26] Addition of only one Lewis base group (carbonyl) to a polyether can significantly lower miscibility pressure in CO₂, an ether-carbonate copolymer will dissolve in CO₂ at lower pressures than that of fluorinated polyether with a comparable number of repeat units.

Johnston and coworkers also studied the solubility of homopolymers and copolymers in carbon dioxide.^[27] The cloud points of various polyether, polyacrylate, and polysilocane

homopolymers and a variety of commercially available block copolymers were measured at CO₂ from 25-65°C and pressure from 1000 to 6000psi. They found the decreasing solubility in the following order for the series: polyfluorooctylacrylate > polypropylene oxide > polydimethylsiloxane > polyethylene oxide > polyacrylates, where, the solubility of polyfluorooctylacrylate is greater than 10wt%, while the polyacrylate is insoluble in the above condition. They related the polymer solubility with the polymer-polymer interaction and surface tension.

McHugh and coworkers studied a series of polyacrylate and poly (vinyl acetate) (PVAc).^[25] The cloud point pressure data at a concentration of 5wt% polymer, polyacrylate and poly vinyl acetate were studied together. PVAc is much more soluble than poly methyl acrylate, even the molecular weight of PVAc is 125000, which is much larger than the molecular of PMA, which is only 31000. The experiment also found PVAc and PMA's cloud point pressure respond differently to the temperature change, at temperature range from 295K to 423K. The cloud point pressure of PMA decreased as the temperature increased, while PVAc's cloud point pressure increased as the temperature increased. Even so, the PVAc's cloud point pressure always much lower than PMA's cloud point pressure. McHugh and coworkers noticed the glass transition temperature of PVAc is 21K higher than that of PMA, which indicated that the stronger polar interactions between acetate groups relative to methyl acrylate groups. PVAc is considered to be more polar than PMA, which helps the formation of a weak association of carbon dioxide and vinyl acetate especially at moderate temperature.^[25]

McHugh and coworkers studied poly(lactide) (PLA), which has been shown to dissolve at high concentration in neat CO₂.^[28] The pressure required to dissolve PLA is higher than that to dissolve PVAc. For PVAc and PLA at 5wt% concentration in CO₂, the required pressure is

70MPa for PVAc, and 140MPa for PLA. Both PVAc and PLA are at 308K condition, and molecular weight (M_w) is about 130000. Because the glycolide functionality are even less CO_2 -philic than PLA, the copolymer of lactide and glycolide are even more difficult to dissolve in CO_2 .

3.0 APPROACH

The proposed approach is to increase viscosity of CO₂ by addition of dilute concentration of a copolymer. To reach this goal, we propose to design and synthesize associating copolymers. The ideal copolymer has two characteristics. The copolymer must contain CO₂-philic groups capable of making the polymer soluble in dense carbon dioxide. The polymer must also contain CO₂-phobic functional groups, which increase the viscosity of CO₂ via viscosity-enhancing intermolecular interactions while not dramatically reducing CO₂ solubility.

The specific goal is to increase the viscosity of liquid CO₂ by a factor of 2-10 in concentration as low as 0.1~1wt%, as determined by Darcy's Law for fluids the low Re flow of through porous media. Fluorinated copolymers were initially evaluated in proof-of concept tests. Non-fluorous polymers were then assessed in an attempt to identify an inexpensive non-fluorous homopolymer that could be subsequently modified to become thickening agents.

3.1 Fluorous CO₂ Thickener

Because the high solubility of fluoroacrylate polymers, it is the first choice in our search for the CO₂ thickeners. Although a high molecular weight polyfluoroalkylacrylate homopolymer could induce a slight increase in CO₂ viscosity, incorporation of the associating group into it can dramatically increase the CO₂ solution viscosity via intermolecular interactions. From all the CO₂ thickeners we investigated, we have found that the fluoroacrylate/styrene copolymer is a promising candidate for thickening carbon dioxide. The fluoroacrylate functionality is highly CO₂-philic, thereby enhancing the copolymer solubility. The styrene is the CO₂-phobic

viscosity-enhancing component. The intermolecular “stacking” of the CO₂-phobic phenyl groups can lead to the formation of macromolecular structures in solution.

The copolymer was bulk-polymerized, rather than solution-polymerized, to attain high molecular weight. There is an optimal composition of the fluoroacrylate-styrene copolymer for thickening carbon dioxide. The 29mol% styrene/71mol% fluoroacrylate was particularly effective in thickening carbon dioxide as observed in falling cylinder viscosity tests. Higher styrene content not only led to significant increases in the cloud point pressure, but also a diminished thickening capacity. It is conjectured that the decrease in thickening may be attributed to the increased intramolecular, rather than intermolecular stacking of the phenyl groups.

We conducted a thorough rheological study of CO₂ solutions containing up to 5wt% of the 29mol% Styrene-71mol% Fluoroacrylate copolymer. This is accomplished with a falling cylinder viscometer with aluminum cylinders of varying diameter. This enables the viscosity-shear rate relationship to be determined. The mobility of thickened carbon dioxide solutions flowing through Berea sandstone is also evaluated. Superficial velocities associated with EOR, 1ft/day and 10ft/day, are used, and increases in viscosity are reflected by increases in pressure drop across the core at a specified flow rate.

3.2 Non-fluorous CO₂ Thickeners

The fluoroacrylate-styrene copolymer was a proof-of-concept copolymer; it is not a feasible candidate for CO₂ thickening in the oil field because of the expense and environmental persistence associated with its fluorine content. Therefore, we also initiated the design of non-

fluorous CO₂ thickeners. The strategy was that we first try to identify highly carbon dioxide soluble polymers that could be later functionalized with CO₂-phobic associating groups. Several promising non-fluorous CO₂ soluble polymers were identified in the literature, including poly(propylene oxide) and poly(vinyl acetate).

Beckman and coworkers have designed and synthesized several CO₂-philic hydrocarbon copolymers composed of (A) monomer 1 (M1) that contributes to high flexibility, high free volume, and weak solute/solute interaction (low cohesive energy density or surface tension), usually M1 shows low T_g, resulting a favorable entropy of mixing for the copolymer as well as weak solute-solute interaction, easing dissolution into CO₂. (B) monomer 2 (M2) that provides specific solute/solvent interaction interactions between the polymer and CO₂, through a Lewis base group in the polymer structure.

Under this guideline, Oxirane/CO₂ copolymers were synthesized, with sterically hindered aluminum catalysts. This is done by copolymerizing propylene oxide (PO), ethylene oxide (EO), or cyclohexene oxide (CHO) with CO₂, incorporating the carbonyl groups into the backbone of polymer. They found PO-CO₂ copolymer with 56% carbonate was less CO₂-philic than a homopolymer of PO, but copolymer with 40% carbonate exhibited miscibility pressures lower than that of the homopolymer. PO-CO₂ copolymer also appeared to be more CO₂-philic than fluoroether polymers. CHO-CO₂ with high chain lengths and a low amount of carbonate units also exhibited very low miscibility pressures in carbon dioxide.^[29]

Guided by such promising results, we decided to investigate the polybutadiene, and all its derivatives. We can buy polybutadiene from Aldrich with different Mw and Mn. We also investigated the hydroxylate ended polybutadiene, and acetate ended polybutadiene, because butadiene is a good candidate for M1, and with low CED, low T_g, high flexibility and high free

volume. While the acetate group is good associating group, combining them together, it may produce a good CO₂ thickener.

3.3 Non-fluorous Homopolymer

In our search for a non-fluorous homopolymer, we need to identify a good base-homopolymer, upon which we incorporate associating groups, make copolymer a good CO₂ thickener. In synthesizing a homopolymer, two characteristics must be attained. First, a CO₂-philic component that increases polymer solubility must be found. Second, there must be an intermolecular associating component that increases solutions viscosity.

The polymers were chosen for synthesis based on their structure and attached groups. The homopolymers were polybutoxyethyl acrylate, PBEA; polyethoxyethyl acrylate, PEEA; polyvinyl ester and polyvinyl acetate. Both PBEA and PEEA were chosen based on their acrylate group. Polyacrylates have been found to be CO₂ soluble because of enhanced interactions between carbonyl moieties. Polyvinyl ester has methyl substitutions making its structure similar to that of Polypropylene oxide. In Polypropylene oxide's case, the methyl substitution on each monomer unit in the chain has a large effect on the solubility. Polypropylene oxide is also CO₂ soluble because of the weak physical segments due to sterical effects and acid-base interactions not being as prevalent. The reason polypropylene oxide is the guide for finding a CO₂ thickener is that polypropylene oxide is the best commercial base material up to date. The better the base the more CO₂-philic a polymer will be. The promising polymer, Polyvinyl acetate has already been found to be CO₂ soluble, but at a high molecular weight. The objective is to determine whether or not polyvinyl acetate can be synthesized at a low molecular weight, using a more

accurate method of polymerization, Atom Transfer by Radical Polymerization (ATRP). If a low molecular weight is achieved, then we need to find out whether its CO₂ solubility is comparable to the CO₂ solubility of Polypropylene oxide.

In summary, the fluoroacrylate-styrene bulk-polymerized random copolymer has exhibited the most promise as a CO₂ thickener. Therefore, a rheological investigation of CO₂-fluoroacrylate-styrene copolymer solutions over a range of flow rates and concentrations was conducted with a falling cylinder viscometry and with a flow-through-porous-media viscometer. Also, to be environmental benign, and feasible in the oil fields, we have been designing and synthesizing different non-fluorous polymers, mainly in acrylate-based and acetate-based polymers.

4.0 THICKENING CANDIDATES

4.1 Fluoroacrylate-styrene Copolymer

Among all the thickeners we tested, fluoroacrylate-styrene copolymer (heptadecafluoroacrylate styrene copolymer) has the most significant viscosity enhancement. The fluoroacrylate functionality is highly CO₂-philic, while the intermolecular " π - π stacking" of the CO₂-phobic phenyl groups associated with the styrene monomer leads to the formation of macromolecular structures in solution.^[30]

4.1.1 Material and Methods

Both styrene and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (HFDA) were purchased from Aldrich. The styrene was distilled under vacuum before use. The heptadecafluorodecyl acrylate and styrene were passed over inhibitor removal columns to facilitate copolymerization. All other solvents and reagents were received from Aldrich, and used without purification.

The polymerization technique is bulk free radical polymerization, with AIBN as initiator. The amount of initiator is about 0.2% mole of monomer. The reaction occurs in a 50 ml glass ampule, in an inert N₂ atmosphere. Specified amounts of HFDA, styrene and AIBN are charged into the ampule. The ampule is sealed and placed in a water bath at 65°C for 12 hours. The reaction products are then dissolved in 1,1,2-trichlorotrifluoroethane. The copolymer is then precipitated in methanol (which is capable of dissolving both monomers, but not the copolymer),

Chemical reaction scheme showing the AIBN-initiated copolymerization of a fluoroacrylate and styrene at 338K.

The reactants are:

- Fluoroacrylate (left): $(\text{CF}_2)_7\text{CF}_3$ attached to an acrylate backbone.
- Styrene (middle): $\text{C}_6\text{H}_5\text{CH=CH}_2$, labeled as the "Styrene Intermolecular Associating Component".

The reaction conditions are AIBN and 338K.

The product is a Copolymer (right), which is a block copolymer containing both fluoroacrylate and styrene units.

4.1.2 3M Fluoroacrylate Styrene Copolymer

25

4.1.3 Random Styrene-FA-x Copolymer

We also tried to synthesize random copolymer of styrene and the Asahi FA-x fluorinated monomer. FA-x is 2-perfluoroalkyl (C6-C16) ethyl acrylate, which is about 10 times cheaper than the Aldrich monomer. We examined both the homopolymer of FA-x and random copolymers of FA-x and styrene.

The synthesis of random Copolymer of FA-x and styrene is similar to the synthesis of fluoroacrylate-styrene copolymer, substituting HFDA with FA-x. We only need to purify the FA-x before use. First, FA-x is washed with 5% NaOH three times, it is washed with distilled water three times, MgSO_4 is added to remove the trace water, then it was put into refrigerator, and then filtered. The synthesis of FA-x homopolymer is the same as the synthesis of copolymer, only use FA-x as monomer, instead of FA-x and styrene.

4.2 Butadiene-Acetate Copolymers

An attempt was also made to synthesize a non-fluorous copolymer composed of two monomers, designed as M1 and M2. M1 is selected from groups that have low cohesive energy, while M2 group should exhibit an intermolecular association with CO_2 .

Polybutadiene has low T_g of about 170K. It is a good candidate as M1 for its low cohesive energy density. Several butadiene-M2 copolymers were studied. M2 can be one of many types of monomer, as long as it has some kind of association with CO_2 , such as Lewis base groups, ethers and acetates. Acetate is a good candidate for M2, forming a carbonyl structure in side chain. Because it is difficult to directly co-polymerize butadiene and acetate, the synthesis

began with polybutadiene. First the polybutadiene was partially dihydroxylized. Second, the dihydroxylized polybutadiene was reacted with acetyl chloride, yielding the butadiene acetate copolymer, Figure 4.2-4.3. Various butadiene : acetate ratios were synthesized. Alternatively, we can first partly epoxylize polybutadiene, then partly hydroxylize polybutadiene, and finally obtain the desired butadiene acetate copolymer via reaction with acetyl chloride, shown in Figure 4.4-4.6.

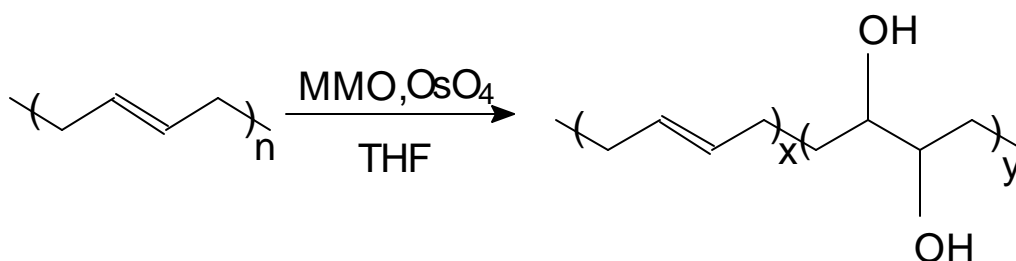


Figure 4.2 Synthesis of partly dihydroxylized polybutadiene

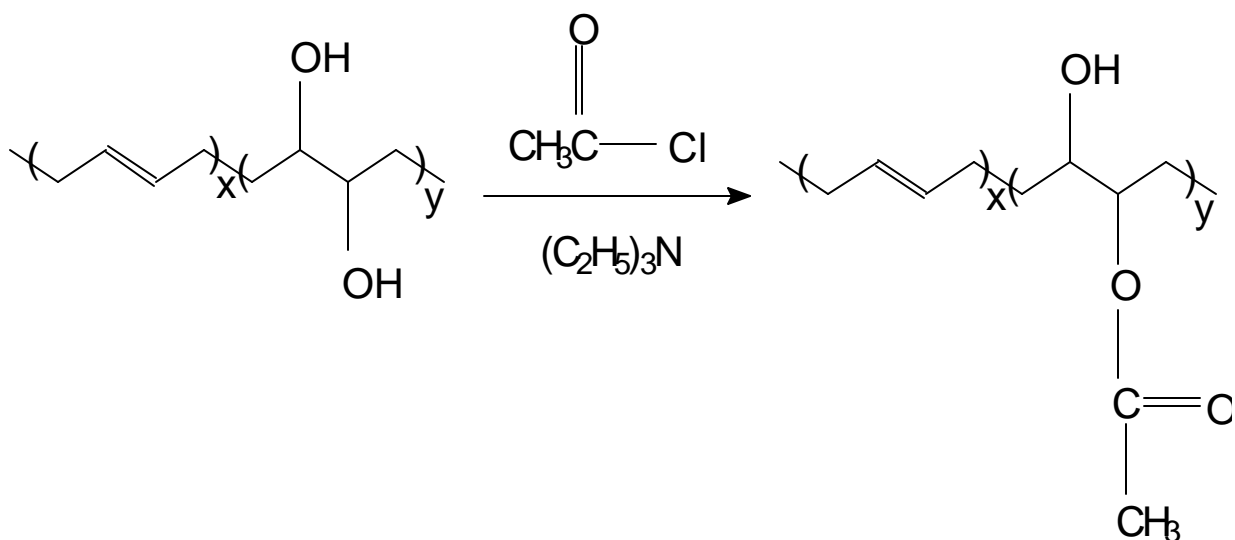


Figure 4.3 Synthesis of partly acetate functionalized dihydroxylized polybutadiene.

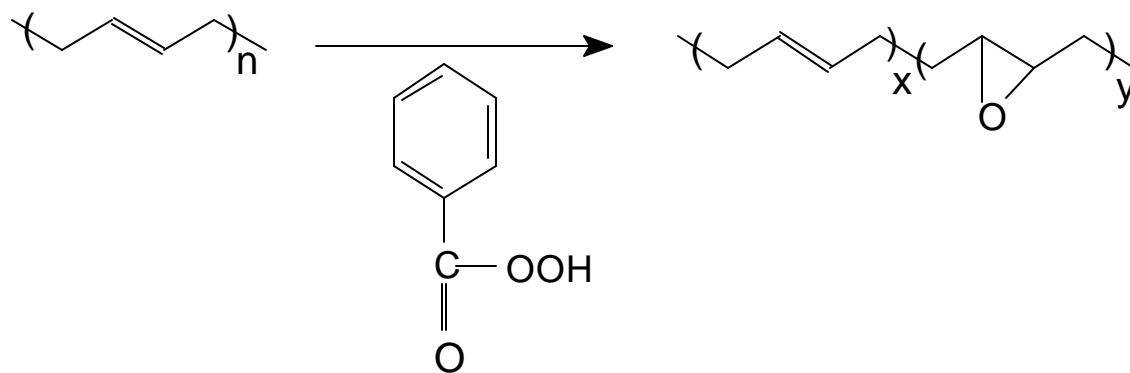


Figure 4.4 Synthesis of partly epoxylized polybutadiene

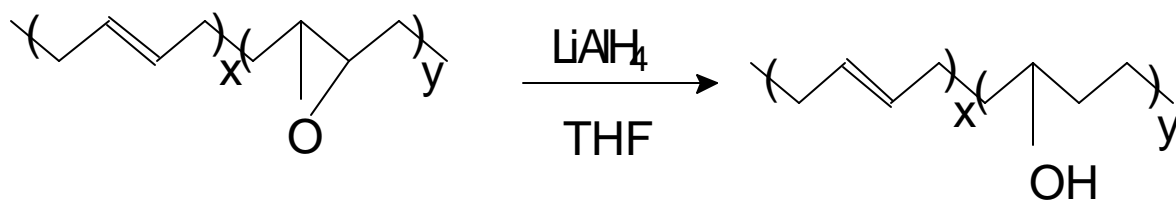


Figure 4.5 Synthesis of partly hydroxylized polybutadiene

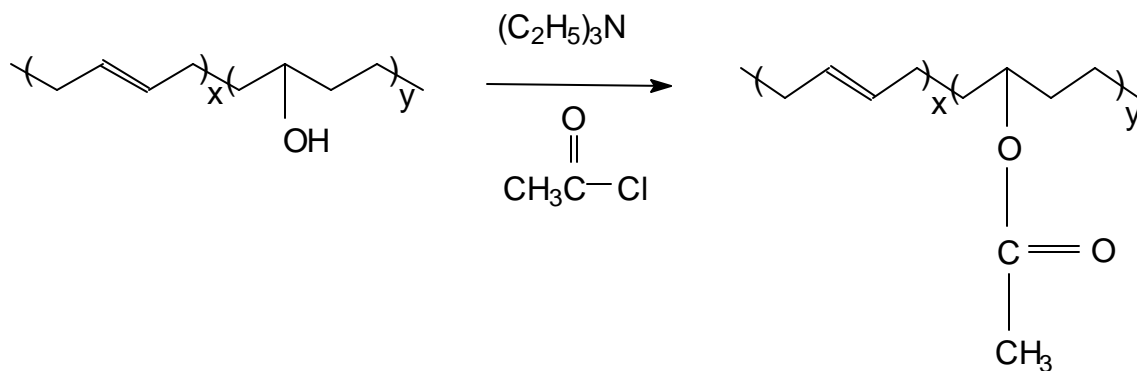


Figure 4.6 Synthesis of partly acetated polybutadiene

4.3 Other Non-fluorous Polymers

In an attempt to identify an inexpensive highly CO₂-soluble polymer (that could subsequently be modified into a thickener), many non-fluorous polymers were evaluated, including poly propylene oxide, polyethoxyethyl acrylate, polybutoxyethyl acrylate, polyvinyl ester, poly vinyl acetate, polymethyl acrylate and poly vinyl formate. Among them, the poly vinyl acetate and low molecular weight poly (propylene oxide) exhibited appreciable CO₂ solubility in our apparatus (rated to 7000psia).

4.3.1 Materials and Methods

All the monomers, solvents and reactants were purchased from Aldrich Chemical Co. Monomers were purified using an inhibitor removal column.

The first method of synthesis, free radical polymerization using azobisisobutyronitrile (AIBN), had the monomer and AIBN mix together in an ampule. They were degassed with N₂ for ten minutes and sealed. Then the ampule was heated in a silicon oil bath for three hours at 60° C. The solubility of the sample was tested with a number of different solvents, including, tetrahydrofuran (THF), methane, and hexane. Then the polymer was precipitated using a solvent that it was very insoluble in. Three purification cycles were done using the Rotavaporator and THF, to clean the polymer and remove any excess monomer. Finally the purified polymer was dried in a vacuum oven for 24 hours.

The second method of synthesis was Atomic Transfer by Radical Polymerization (ATRP). Although ATRP was used for all homopolymers, two different types of purification methods were used.^[31, 32] For example, the application of ATRP to the homopolymerization of 2-hydroxyethyl acrylate was previously reported.^[31] It was determined that through ATRP the polymerizations exhibit first order kinetics and the molecular weights increase linearly. In addition, the polydispersities remain low throughout the polymerization. For polybutoxyethyl acrylate, polyethoxyethyl acrylate, polyvinyl ester, ATRP was done using following reactants: Monomer, Initiator: Methyl 2-bromopropionate, Catalyst: CuBr, and Ligand: 2-2' bipyridine with ratios M:I:Cu:L = 50:1:1:2. These reactants were added to the ampule and degassed for ten minutes with N₂. The ampule was sealed and placed in the oil bath for three hours at 90° C. The second ATRP method was used in order to try to control the molecular weight of polyvinyl acetate. Synthesis was done using the following reactants: Monomer, Initiator: CCl₄, Catalyst: FeAc₂ and Ligand: N, N,N'N'',N'''-pentamethyldiethylenetriamine (PMETA) with ratios M:I: C: L=15:1:1:1. Three freeze-pump-thaw cycles were performed and the flask was sealed under the vacuum and placed in the oil bath for three hours at 60° C. The polymer was purified through an Al₂O₃ column. It was washed twice with THF and then dried in a desiccator overnight.

4.3.2 Characterization

The weight average Mw, number average Mn, and polydispersity index were evaluated using Gel Permeation Chromatography (GPC). GPC separates molecules in solution by their effective size in solution. In this project, the sample had to be soluble in THF in order to be analyzed, because THF had been selected as the sole solvent to be used in

the GPC. Once inside the GPC, the dissolved resin is injected into a continually flowing stream of solvent. The solvent, mobile phase flows through highly porous, rigid particles (stationary phase) tightly packed together in a column. The sizes of the particles pores are controlled and available in a range of sizes. The distribution of chain lengths and therefore molecular weight of the polymer are dependent on the method of synthesis. A free radical polymerization, for example, may produce a polymer with a very broad distribution of chain lengths and high molecular weights. The molecular weights of the THF-insoluble fluorinated copolymer were determined by American Polymer Standards Corporation. This company employed fluoruous solvents in their GPC.

5.0 SOLUBILITY APPARATUS

The phase behavior studies of our CO₂ thickeners are performed at room temperature, using a high pressure, variable-volume, windowed cell (D. B. Robinson Cell), with a cylindrical sample volume, as Figure 5.1. The system is rated to 7000psi and 180°C.

Isothermal compression and expansions of sample/CO₂ mixtures of specified overall composition are used to determine polymer solubility via cloud point determination. The procedure is as follows. First, the CO₂ thickener sample is added into the sample chamber along with several stainless steel mixing balls. Then high-pressure carbon dioxide is displaced into the positive displacement pump with a gas booster. The carbon dioxide liquid is then injected into the sample volume by a positive displacement pump as the sample volume is expanded at the same volumetric rate via the withdrawal of the overburden oil. Therefore, one can add a desired amount of liquid carbon dioxide into the sample volume in a well-controlled, isothermal, isobaric manner.

After the high-pressure carbon dioxide is injected into the sample volume, the inlet valve to isolate the sample volume from high-pressure carbon dioxide is closed. The pressure of the sample volume can be increased by pumping the overburden fluid into the windowed cell, decreasing the sample volume. Mixing with the stainless steel balls is accomplished by rocking the view-cell until the sample is totally dissolved. The pressure of the sample volume is reduced by expanding the sample volume at the same time the overburden fluid is withdrawn at a high flow rate, until visual observations of the initial appearance of a second phase occurred. Then the sample volume pressure is increased and the cell rocked until a transparent solution is viewed again. The overburden fluid is then withdrawn at a very low flow rate, providing a more

accurate cloud point pressure determination. This procedure is repeated several times, yielding an average cloud point pressure. The cloud point pressure is the minimum pressure required to keep the thickener dissolved in carbon dioxide. Below this pressure, the solution becomes a two-phase system.

We can conduct cloud point experiment with different overall compositions. The results can be presented in a pressure-composition diagram at the temperature of interest.

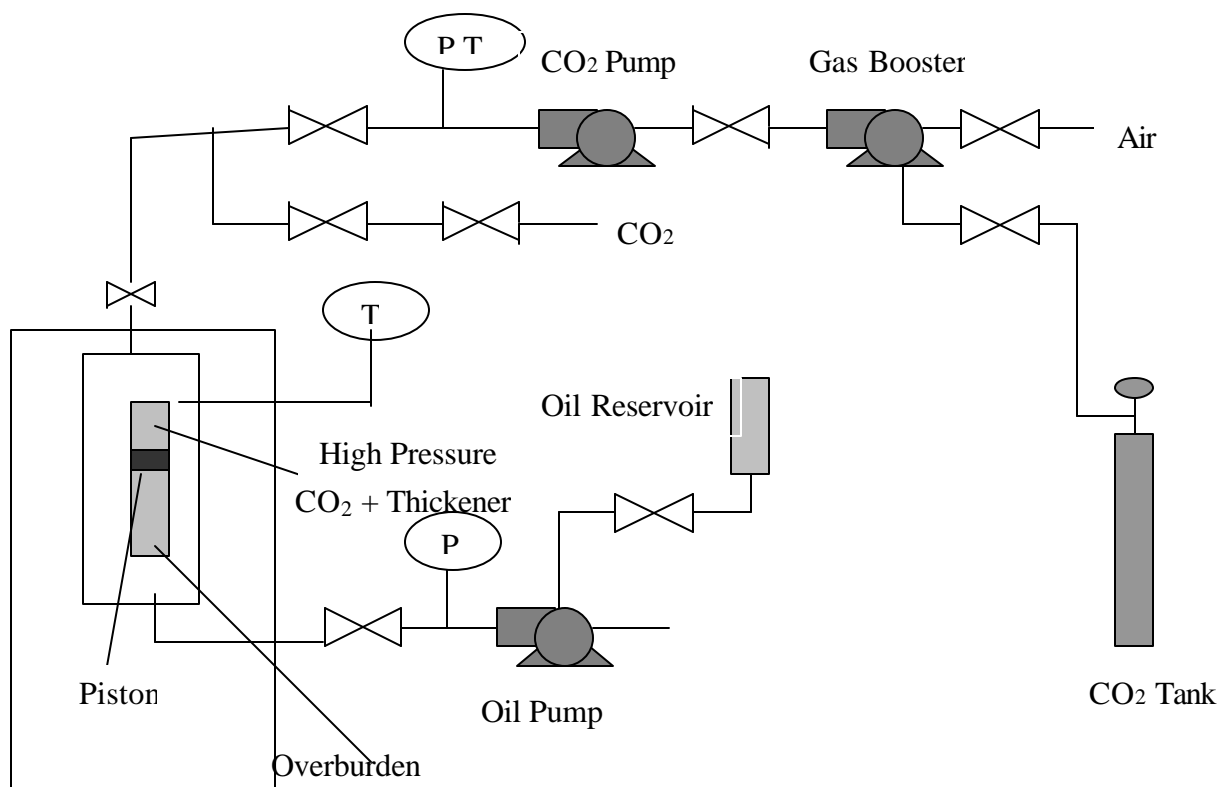


Figure 5.1 High pressure, variable volume, windowed cell (D. B. Robinson Cell)

6.0 FALLING CYLINDER VISCOMETER

The simplest and quickest test for estimating low pressure and high pressure fluid viscosity is falling object viscometry. Beginning with Lawaczeck,^[33] it has been widely studied and applied in rheology studies.^[30, 34-40]

Falling cylinder viscometer is also a useful tool for high pressure viscometry when a relatively low viscosity single phase exists. Both petroleum engineering and chemical engineering investigators have used various versions of falling object viscometers in their studies of carbon dioxide-rich systems.^[41, 42]

We used a thick-walled, precision, hollow glass tube as the viscometer [D.B. Robinson] and a series of close clearance aluminum cylinders (Figure 5.1) for viscosity measurement. The hollow glass tube is the same tube used in phase behavior studies. The falling cylinder dimension is shown in Table 6-1.

For carbon dioxide or carbon dioxide-thickener solution viscosity measurements, the following procedure is used. The aluminum cylinder is moved to the top of the vertical, transparent tube, which is filled with the high pressure fluid, by rapidly inverting the cell. The cylinder falls down. Because of the narrow annular gap bounded by the aluminum cylinder wall and glass cylinder wall, the falling aluminum cylinder rapidly attains its terminal velocity. Velocity is calculated by measuring the falling time between the distance of two locations, Figure 6.1.

Table 6-1 Falling cylinder viscometer dimensions

Glass tube ID		Cylinder Material	Cylinder Gravity (g/cm ³)	Cylinder Length (inch)	Cylinder Diameter (inch)	Gap (inch)	Cylinder Length/Gap
ID(inch)	Length (inch)						
1.2500	8	Aluminum	2.7	0.8268	1.2450	.005	165
					1.2438	.0062	133
					1.2428	.0072	115
					1.2399	.0101	82
					1.2339	.0161	51
					1.2311	.0189	44
					1.2293	.0207	40
					1.2269	.0231	36

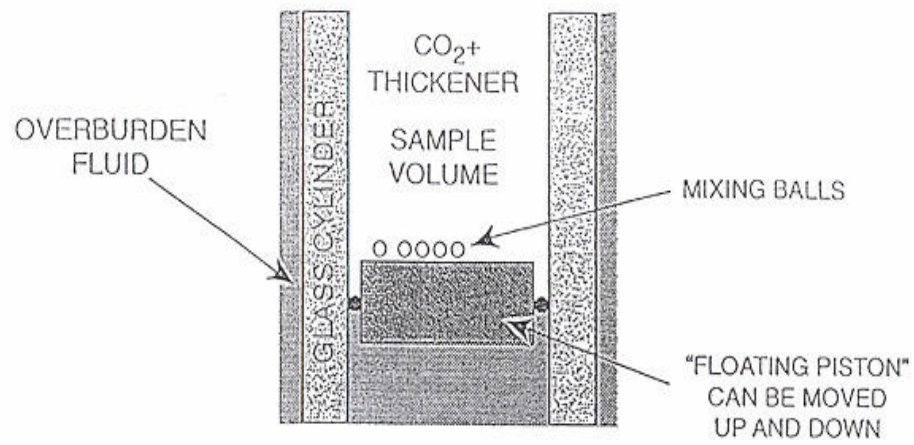
In the region of Stokes' law

$$m \propto \frac{(r_c - r_f)}{V_c}$$

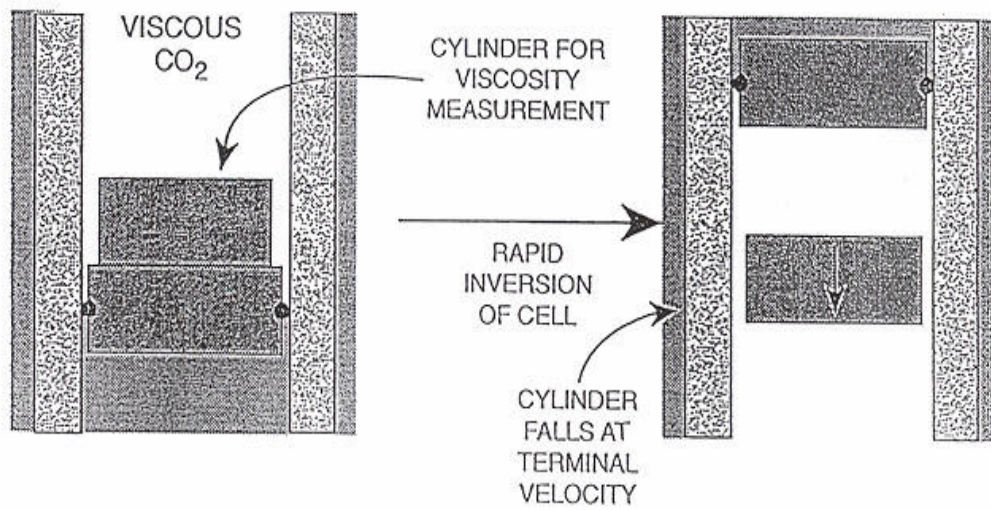
The viscometer constant is defined as

$$K = \frac{m \cdot V_c}{(r_c - r_f)}$$

For this equation to be used accurately, the annular flow must be laminar. The formula cannot fit in the turbulent region. With our D.B. Robinson Cell, we studied the falling cylinder friction factor, Reynolds number and viscometer calibration constant.



SOLUBILITY ARRANGEMENT



VISCOSITY MEASUREMENT

Figure 6.1 Viscosity measurement

6.1 Friction Factor

The friction factor f is affected by the nature of the flow (laminar or turbulent), contraction, expansion and imperfections in the hollow cylinder or falling cylinder. The experiment calibration constant is usually smaller than theoretically calibration constant, owing to contraction, expansion, and imperfection losses. Because these effects and the effect of turbulence cannot be treated mathematically, dimensional analysis was used to develop a correlation to account for these effects. The friction factor is

$$f = \frac{4 Fg \cdot Gc \cdot De}{\rho \cdot d^2 \cdot r_f \cdot V_c^2 \cdot l}$$

When only laminar flow occurs, the friction factor is: $f = 16/N_{Re}$

$$\text{Here, } N_{Re} = \frac{De \cdot V_c \cdot r_f}{\mu}, \text{ Reynolds number}$$

Fg : force of gravity on the falling body, g-force

Gc : universal gravitational constant, g-mass-cm./g-force-sec²

De : equivalent diameter of the viscometer tube-body annulus, cm

$$De = \sqrt{2} \cdot d \cdot \sqrt{\ln \frac{D}{d} - \frac{D^2 - d^2}{D^2 + d^2}}$$

r_f : fluid density, g/cm³

L : length of the falling cylinder, cm

V_c : terminal velocity of the falling cylinder, cm/s

μ : absolute viscosity, poise

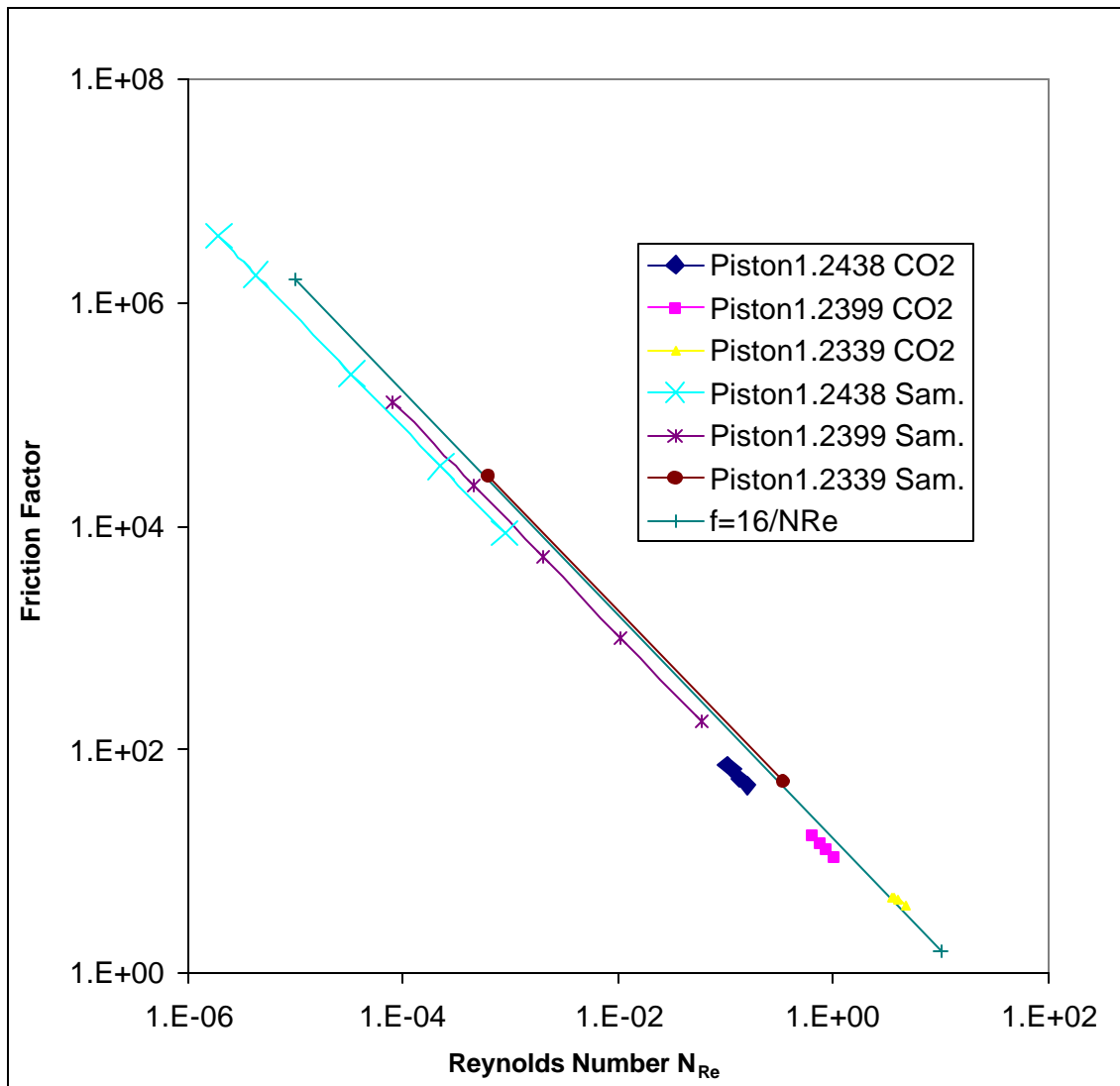


Figure 6.2 Friction factor vs. Reynolds number

From our experiment data, in Figure 6.2, all our experiments, the slope of the line is constant, and equal to -1 , indicating all appreciable frictional effects are laminar. The difference between our experiment lines and $f = 16/N_{Re}$, are due to the contraction, expansion and imperfection losses.

6.2 Reynolds Number

Lohrenz and coworkers^[34,35] studied calibration constants in laminar region and calibration constants in turbulent region, they found the critical N_{Re} is about $0.13 \sim 1.0$. They concluded that when the Reynolds number is close to 0.1 , all frictional effects may be assumed to be laminar.

From result of our data, the Reynolds number of most falling cylinder are between $0.1 \sim 1.0$, for pure CO_2 . For the more viscous polymer solutions, the Reynolds number is expected to be smaller.

6.3 Theoretical and Experimental Calibration Constants

We can assume that the neat CO_2 solution or dilute polymer solution is Newtonian, so,

$$m = K \frac{\mathbf{r}_c - \mathbf{r}_f}{V_c}$$

Then, we can compare the experimental calibration constant K with the theoretical calibration constant, ignoring the resistances because of non-ideal falling.

In our falling cylinder viscometer, we used neat CO₂ as our fluid, at 297K and 3000psi. Because both the density and viscosity of carbon dioxide are known at these conditions, the calibration constant for a cylinder can be determined if the terminal velocity is measured.

$$K = \frac{\rho V_c}{r_c - r_f}$$

We can also determine the theoretical calibration constant from the size of the falling cylinder and the hollow cylinder:

$$K = \frac{r_c g}{r_c J' - 2K'}$$

Where,

$$J' = - \frac{4}{(r_i^2 - r_c^2) + \ln \frac{r_c}{r_i} (r_i^2 + r_c^2)}$$

$$K' = \frac{-2r_c - (r_i^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_i)}}{r_i^2 - r_c^2 + \ln(r_c/r_i)(r_i^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_i)}$$

In Figure 6.3, the diagonal line is the reference line if experimental calibration constant is equal to theoretical calibration constant. The vertical line segment is theoretical “error bar” associated with the machining tolerance of the falling cylinder surface, ± 0.00015 inch difference from the average of the diameter. The horizontal line segment is the experiment calibration constant error associated with the range of terminal velocities measured for neat carbon dioxide.

The experimental calibration constant is reasonably close to the theoretical constant. These results (which are typically not reported for high pressure viscometers) show that the theoretical and experimental values of the viscometer constant agree to within 50%.

This difference may be attributed to imperfections in the aluminum cylinder, the absence of hemispherical heads to the cylinders, non-coaxial descent of the cylinder and/or cylinder rotation.

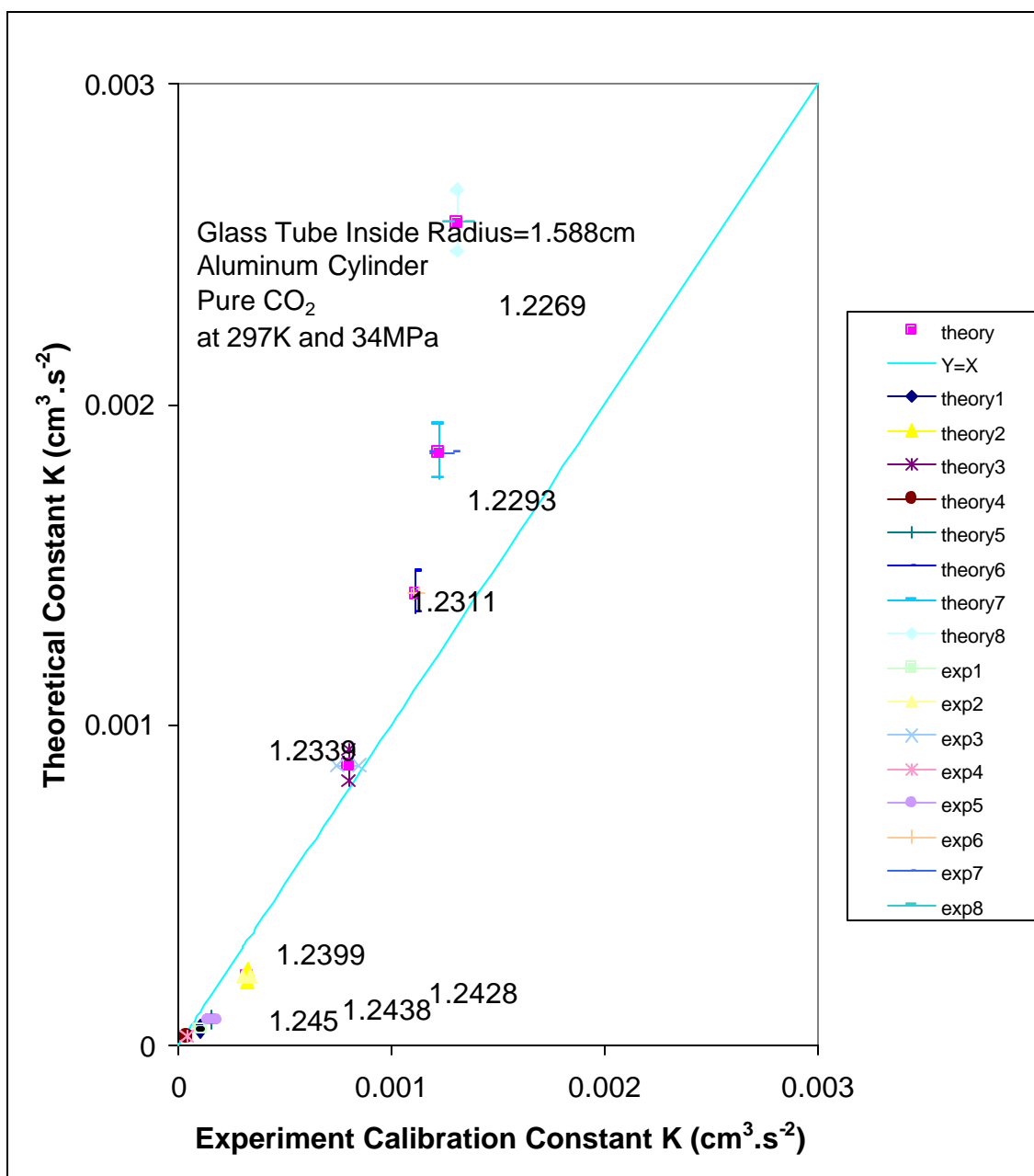


Figure 6.3 Experiment calibration constant vs theoretical constant

7.0 FLOW-THROUGH-POROUS-MEDIA VISCOMETER

The most meaningful measure of carbon dioxide solution viscosity for EOR is associated with the mobility of the fluid flowing through porous media at superficial velocities comparable to those attained in petroleum reservoirs. The ability for thickened carbon dioxide to flow through sandstone at flow rates that occur in the oil field is best measured by displacing thickened carbon dioxide through sandstone cores at the appropriate superficial velocity. A clean, homogeneous Berea sandstone core [American Stone] is used to simulate the performance of CO₂ flooding in a sandstone reservoir.

7.1 Experimental Apparatus

The neat or thickened carbon dioxide is prepared in the same manner as described in the solubility experiments. The objective of the experiment is to displace a single phase fluid through the sandstone core at a constant flow rate. The pressure of the thickened carbon dioxide is maintained at a high enough pressure to ensure a single phase of fluoroacrylate-styrene copolymer-carbon dioxide solution, for polymer concentrations up to 2wt%.

Fluid viscosity can be determined with Darcy's law for the flow of a Newtonian fluid through porous media in the creeping flow regime.

$$\frac{\Delta P}{L} = \frac{\nu \cdot \mu}{D}$$

Where, v is velocity of the fluid flow through the core, μ is absolute viscosity of the fluid, D is permeability, and L is the length of the core. Experiments of neat carbon dioxide can be performed to determine the permeability. Using this permeability value, the viscosity of thickened carbon dioxide solutions can be determined simply by measuring pressure drop. The pressure drop over distance is proportional to the fluid viscosity. Because the same core was used for the viscosity of thickened CO₂ to neat CO₂, the ratio of the viscosity of thickened CO₂ to neat CO₂ was estimated as the ratio of the respective pressure drops along the length of the core.

$$\frac{\mu_{\text{copolymer solution}}}{\mu_{\text{CO}_2}} = \frac{(\Delta P / L)_{\text{copolymer solution}}}{(\Delta P / L)_{\text{CO}_2}}$$

In our experiments, Figure 7.1, the thickened carbon dioxide was prepared in the Robinson cell while the porous media and tubing were charged with neat carbon dioxide. The thickened carbon dioxide was then displaced from the sample volume toward the porous media. The volume available for the core effluent was being expanded at the same volumetric rate that thickened carbon dioxide entered the core, resulting in well-controlled, continuous flow through the core. The pressure drop through the core was monitored continuously as the carbon dioxide solution flowed through the core at a superficial velocity of either 1 or 10 ft/day, which are the typical flow rates in the field. To study the very high flow rate effect on the thickening ability, we also simulate the flow rate at 50 and 80ft/day.

All flow lines, internal volumes and pressure tap volumes for the differential pressure transducers are kept to a minimum so that accurate flow data can be obtained. There are four pressure taps, as shown in Figure 7.1, that enable the pressure drop along each third of the core

to be determined. This facilitates the detection of polymer retention at the entrance of the core, which would be evidenced by a higher pressure drop in the first third of the core than the pressure drops in the other two thirds.

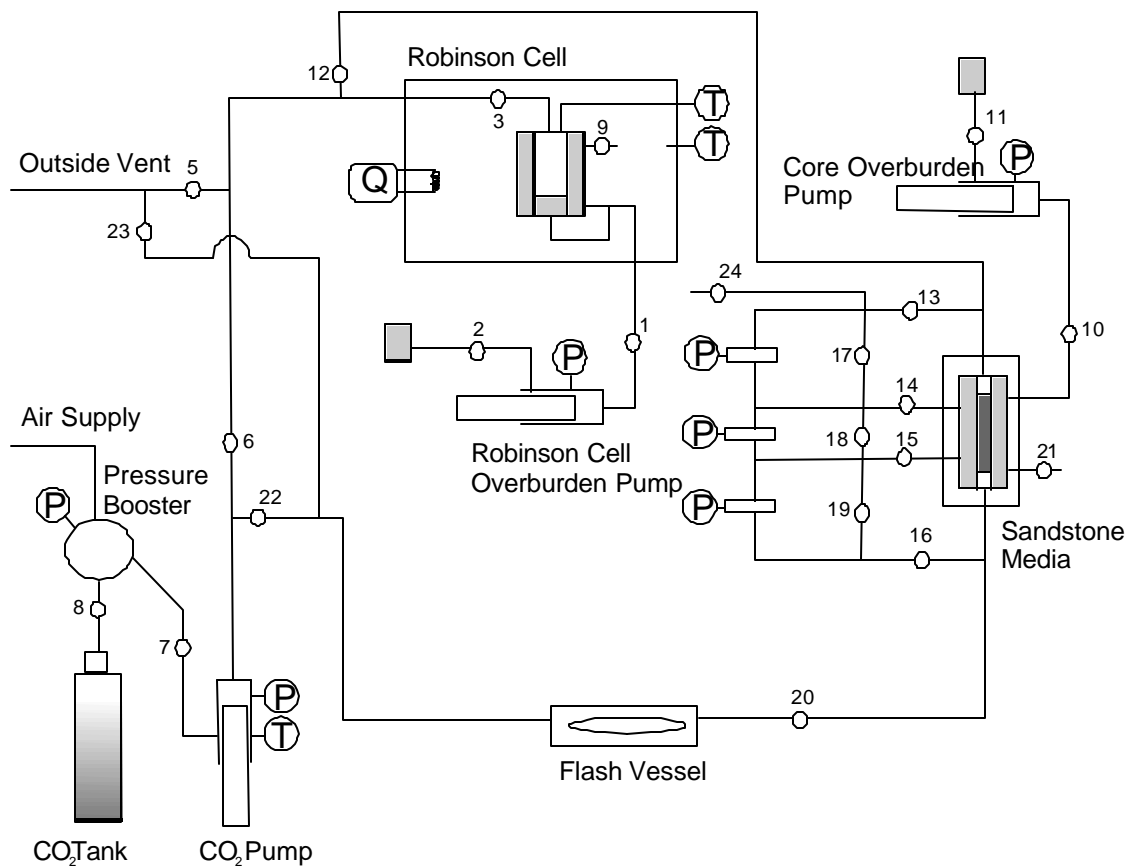


Figure 7.1 Permeability apparatus

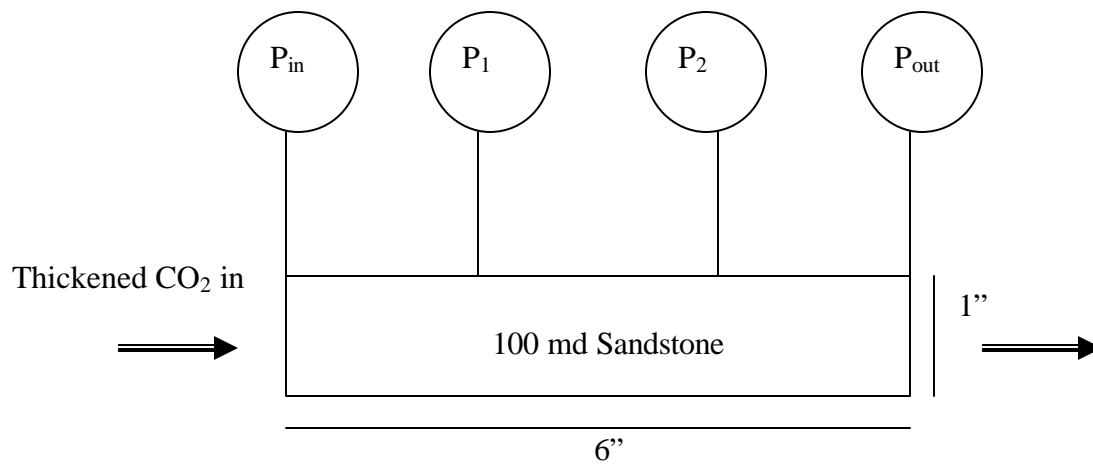


Figure 7.2 Berea sandstone core

7.2 Berea Sandstone Core

Berea sandstone core is manufactured by American stone Co., produced from Cleveland Quarries. The details of sandstone core are shown in Figure 7.2. The core has length of 6 inches and roughly 100 md permeability. The core sample is held within a rubber sleeve in core holder by confining or radial overburden pressure, which is usually 500 psig higher than work pressure. The radial confining pressure simulates reservoir overburden pressure and eliminates the possibility of annular flow of the fluid around the core.

7.3 Core Holder

The core holder is manufactured by Temco. Inc. The pressure rating is 15,000 psig. As illustrated in Figure 7.3, core holder have four pressure ports, all are connected to 1/8" NPT fittings. Overburden pressure port is also 1/8" fitting, at the bottom of core holder. Silicon oil is used as overburden fluid, which clamp strongly around the sleeve, to avoid leaking of carbon dioxide. There are 4 pressure taps; two in the inlet and outlet, the other two are at the top, connected into the middle of the core holder via fittings. At inlet and outlet, long and short retainers with o-rings are used to prevent the leak of silicon oil.

7.4 Pressure Transducer

Given the short length of the relatively high permeability core, 6 inches and 100 md respectively, and the low viscosity of carbon dioxide or thickened carbon dioxide, these are high pressure, low pressure drop experiments.

To meet our situation, our pressure transducer is manufactured by Validyne engineering corp. We select DP303 model, which is designed for very low wet-wet differential pressure measurement in fluid systems involving high line pressure up to 5000psig. In different superficial velocity and different polymer concentration, we use different diagrams, with differential pressure range from 0.125 psid to 0.5 psid.

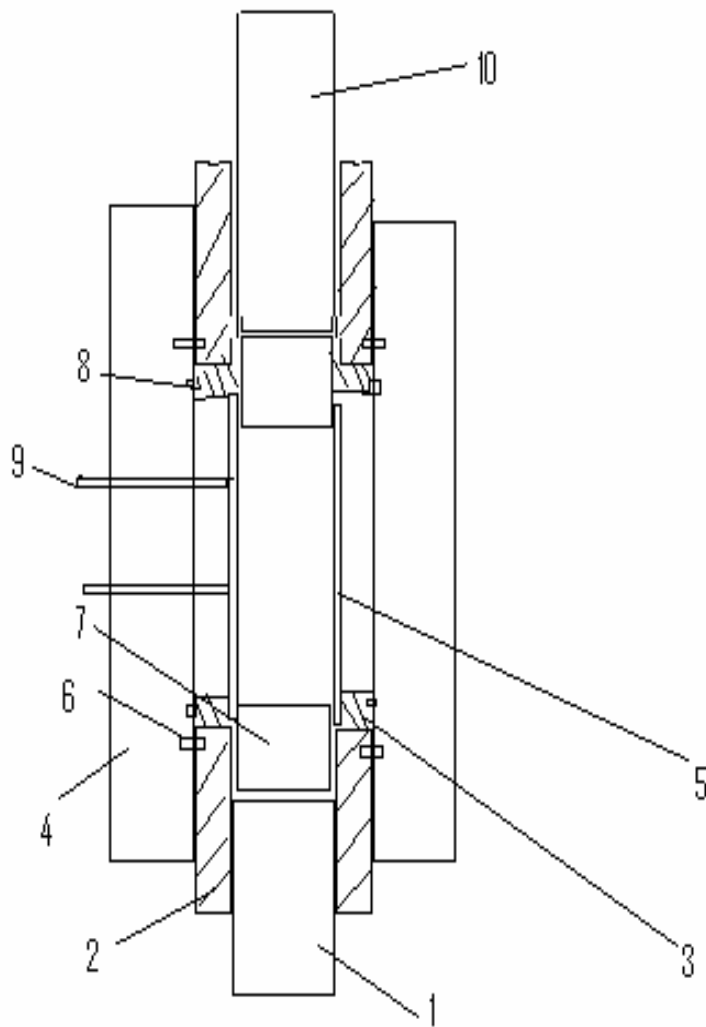


Figure 7.3 Core holder

- | | | | | | |
|---------------|------------|--------------|-------------------|-----------|----------|
| 1. Retainer | 2. End cap | 3. Ferrule | 4. Body | 5. Sleeve | 6. Screw |
| 7. Dist. Plug | 8. O-ring | 9. Connector | 10. Long retainer | | |

8.0 FLUORINATED POLYMER RESULTS

8.1 Solubility Results

8.1.1 Fluoroacrylate Homopolymer and Fluoroacrylate-styrene Copolymer

The fluoroacrylate-styrene copolymer is easily dissolved in liquid carbon dioxide, and the mixture of copolymer and CO₂ is transparent and stable. As expected, the solubility of fluoroacrylate-styrene copolymer in CO₂ does depend on the composition of the copolymer. As shown in Figure 8.1, cloud point experiments at 297 K indicate that the solubility of the polymers decreases with increasing styrene content in the polymer chain.

Compared to polyfluoroacrylate homopolymer, fluoroacrylate-styrene random copolymer needs slightly higher pressure to be dissolved in carbon dioxide, as shown in Figure 8.2. The higher molecular weight and higher styrene content of the copolymer both contribute to the diminished solubility. The molecular weights and PDI is shown in Table 8-1. The number-, weight- and Z-average molecular, M_n , M_w and M_z , respectively, were determined using gel permeation chromatography [American Polymer Standards Corporation].

Table 8-1 Molecular weights of fluoropolymers

	Mn	Mw	PDI	Mw/RU	RU #
Fluoroacrylate-styrene copolymer	539600	880200	1.63	622.32	867
Polyfluoroacrylate homopolymer	86200	254000	2.95	518.17	166
	232000	557000	2.40	518.17	448

8.1.2 Styrene-FA-x Copolymer Solubility

The result of random styrene-FA-x Copolymer is not promising, both the homopolymer and copolymer cannot dissolve in CO₂ well, although both swell significantly in pure CO₂ at 5000psi. The mixture of homopolymer and CO₂ is kind of transparent, below the pure CO₂ phase. The mixture of copolymer and CO₂ is opaque even at 6000 psi. After depressurization, no foam, no gel appeared in both cases.

Therefore the FA-x, a perfluoroalkyl ethyl acrylate, is not CO₂-philic enough. This is in agreement with previous observations that acrylates are more carbon dioxide-soluble than methacrylates or ethacrylates.

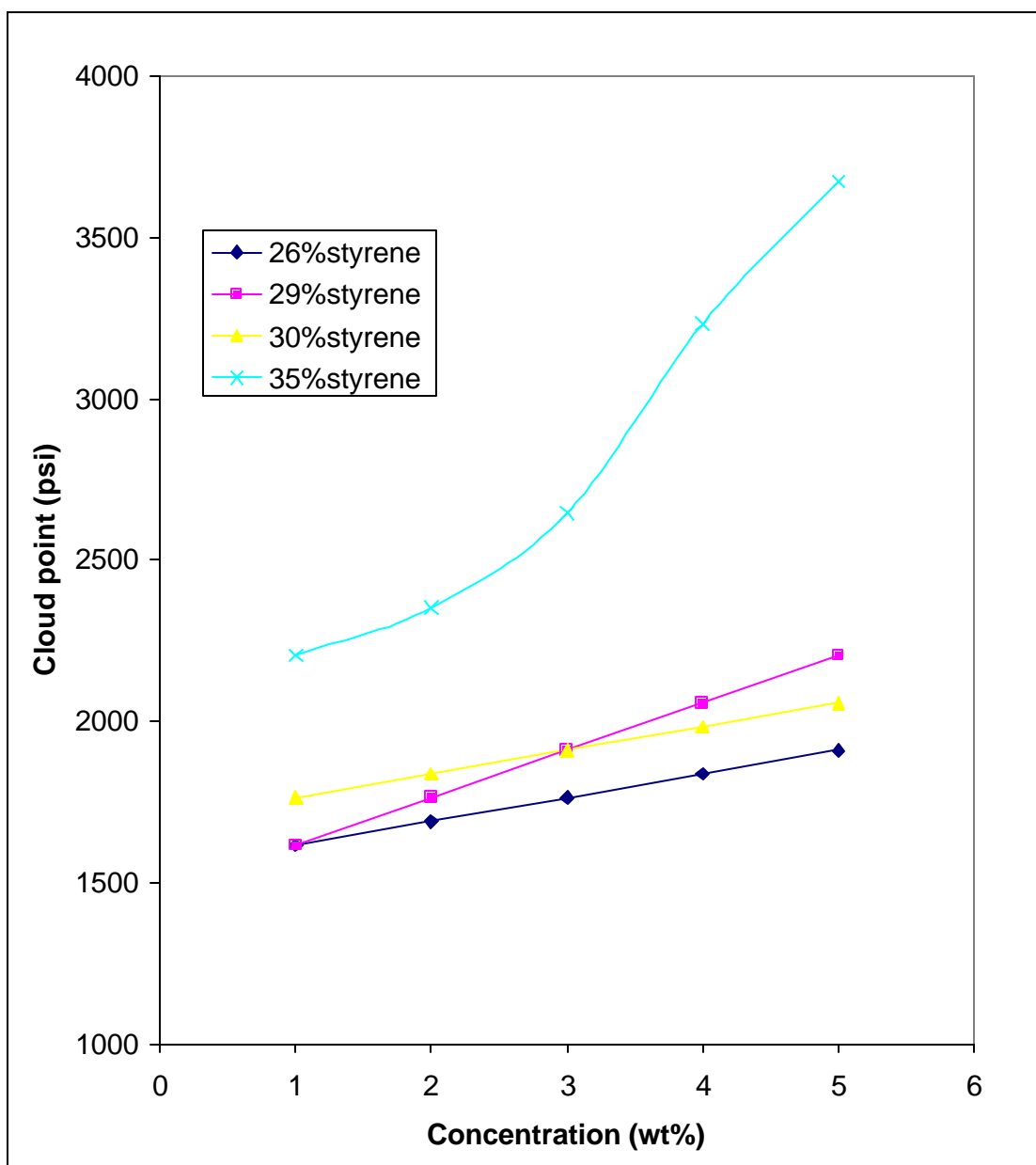


Figure 8.1 Fluoroacrylate-styrene copolymer cloud point vs concentration (T=297K)

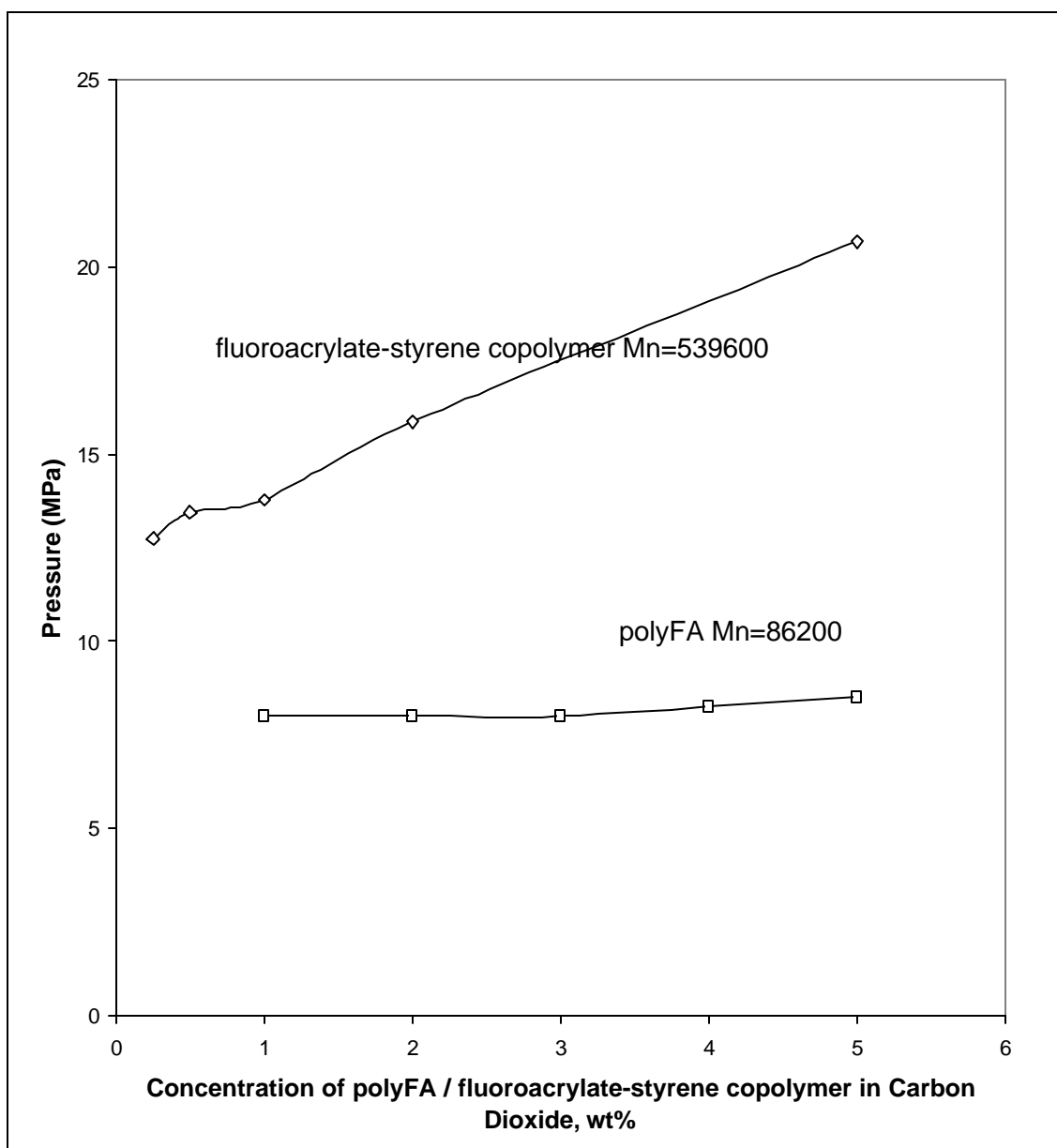


Figure 8.2 Solubility of polyFA and fluoroacrylate-styrene copolymer in carbon dioxide at 298K

8.1.3 Temperature Effect on the Fluoroacrylate-styrene Copolymer Solubility

The fluoroacrylate-styrene random copolymer is soluble in dense carbon dioxide at concentration up to 5wt% at 298K, 323K, 348K and 373K, as illustrated in figure 8.3. The cloud point curve shifted toward higher pressure with increasing concentration and temperature.

The cloud point pressure at any given temperature must be contrasted with the minimum miscibility pressure, MMP, at the same temperature to establish the solubility of the copolymer at reservoir conditions. For example, consider a carbon dioxide miscible project with a minimum miscibility pressure of 18 MPa (2616 psia). Figure 8.3 indicates that at a temperature of 298 K and a pressure of 18 MPa, roughly 3wt% of the copolymer could be dissolved in CO₂; more than enough to significantly thicken the CO₂. At a reservoir temperature of 323 K and a pressure of 18 MPa, about 0.5wt% of the copolymer could be dissolved in CO₂; roughly the lowest amount of copolymer needed to make a significant (e.g. doubling) increase in CO₂ viscosity. At a pressure of 18 MPa and 348 K or 373 K, the solubility of the copolymer in CO₂ would be much less than 0.25wt%; insufficient to induce an appreciable viscosity change.

If greater copolymer solubility is required at the reservoir conditions than is possible with the 79%fluoroacrylate-21%styrene copolymer with a number average molecular weight of 540,000, then a copolymer of comparable molecular weight with a slightly greater fluoroacrylate composition and/or a lower molecular weight would be required^[4.29], thereby making the copolymer more CO₂ soluble. This modification would reduce the thickening capability of the copolymer, however, and a slightly greater concentration of the copolymer would be required to attain a desired level of viscosity.

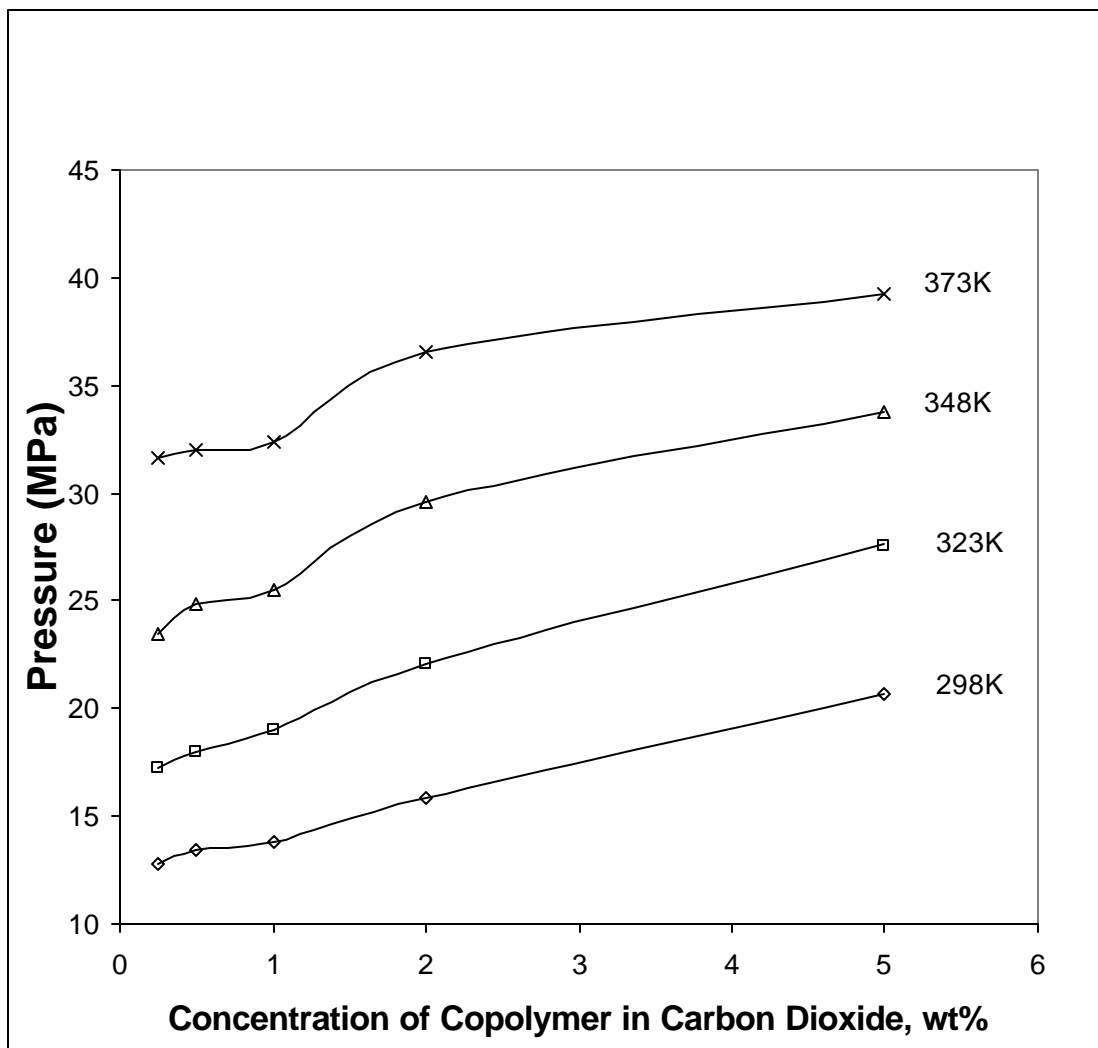


Figure 8.3 Effect of Temperature on the solubility of the fluoroacrylate-styrene copolymer in carbon dioxide

8.2 Falling Cylinder Viscometer Results

8.2.1 Aldrich Fluoroacrylate-styrene Copolymer

From falling cylinder viscometer, all these copolymer can increase CO₂ viscosity by several orders at relatively low concentration. After we found the best relative viscosity increase of 29mol%Styrene-71mol%FluoroAcrylate copolymer, we tested it extensively, with different falling cylinders and different copolymer concentrations. For our best fluoroacrylate-styrene copolymer (29mol% styrene), the relative viscosity of CO₂ solution ($\frac{h_{so \ln.}}{h_{CO_2}}$) is much enhanced, from 2 to 200 times, relative to concentration from 0.2wt% to 5wt%. Because the viscosity is strongly related to shear rate, so, we examined the relative viscosity with different falling cylinder size, see the Figure 8.4.

From the figure, we can see, the viscosity of CO₂ is enhanced more than 200 times in 5wt% copolymer-CO₂ solution, and even in 1wt% solution, the viscosity of CO₂ was increased several times. In lower concentration, 0.2wt% or 0.1wt%, there is still discernible viscosity increase at high shear rates. This viscometer is not suited for the determination of the relative viscosity at the low shear rates associated with creeping flow through porous media (10s⁻¹). Further, the results (based on a Newtonian fluid assumption) illustrated in Figure 8.4 clearly indicate that the fluid is not Newtonian. Therefore, a power law model description of the fluid was derived.

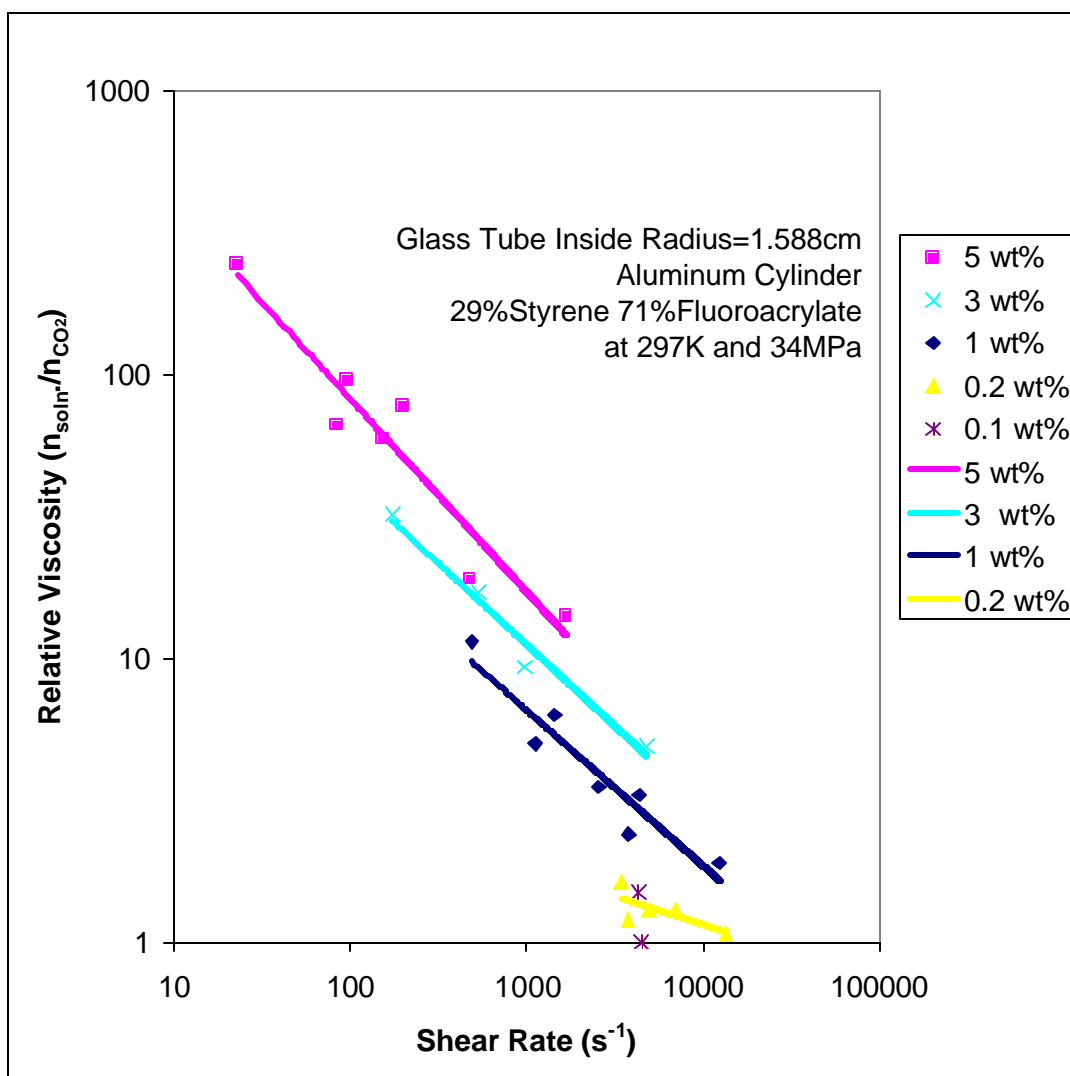


Figure 8.4 Relative viscosity vs shear rate

8.2.2 3M Fluoroacrylate-styrene Copolymer

Encouraged by the 29mol% styrene fluoroacrylate-styrene copolymer, we also investigated 3M fluoroacrylate-styrene copolymer, substituting Aldrich fluoroacrylate with 3M fluoroacrylate as monomer. From Fig. 8.5, the result is quite promising. The thickening ability of the 29mol%styrene-71mol%Fluoroacrylate(3M) copolymer is similar to that of Aldrich fluoroacrylate-styrene copolymer.

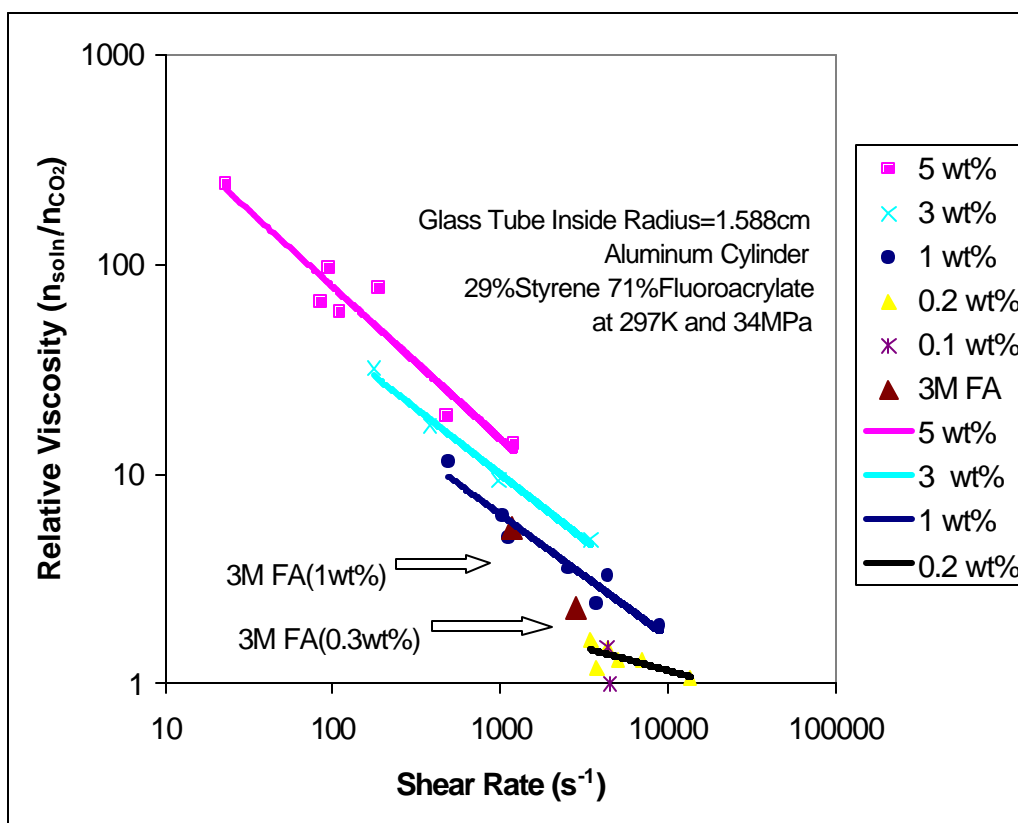


Figure 8.5 Relative viscosity vs. shear rate (3M copolymer)

8.2.3 Temperature Effect on the Fluoroacrylate-styrene Copolymer Thickening Ability

Figures 8.4 and 8.5 indicate that the 29% styrene fluoroacrylate-styrene copolymer has good thickening capacity at ambient temperature, 297 K. Reservoir temperatures extend to 393 K, however. Literature^[43] indicated that there may be a temperature effect on the properties of the atoms in the regions of intermolecular contact via stacking of the phenyl groups. The change in temperature may influence the strength and geometry of interactions, which may result in the change of local molecular environment. This may affect the π - π stacking capacity and thickening capability of the fluoroacrylate-styrene copolymer. Because the majority of CO₂ flooding projects are conducted in reservoirs at temperatures between 25~100°C, we tested the fluoroacrylate-styrene copolymer thickening ability over this temperature range. The fluoroacrylate-styrene copolymer thickening capacity was determined using the 1.2428" diameter falling aluminum cylinder at temperatures of 25°C, 50°C, 75°C and 100°C. Table 8-2 indicates that the temperature doesn't have significant effect on the π - π stacking phenomena.

Table 8-2 Temperature effect on the solution relative viscosity

Temperature (°C)	The fluoroacrylate-styrene copolymer concentration	
	1 wt%	0.3 wt%
25	2.3	1.5
50	2.3	1.5
75	2.1	1.5
100	1.9	1.4

8.2.4 Non-Newtonian Fluid

With the assumption of the polymer/CO₂ solution fit the power-law model (Appendix B), we can get the power law model constants from the experimental falling cylinder terminal velocity, with the minimum difference between calculated velocity and experimental velocity, which is shown in Table 8-3.

Table 8-3 Experimental falling cylinder terminal velocity Unit: cm.s⁻¹

Rc	5wt%	3wt%	1wt%	0.2wt%	0.1wt%
1.245				0.04997	0.06
1.2438	0.0023 0.004104	0.00479	0.03022 0.01325	0.093	
1.2428	0.00388	0.01356	0.03597	0.174	0.15
1.2399	0.02536 0.004945	0.05091	0.1957 0.1334	0.362	
1.2339	0.015		0.35	1.08	
1.2311	0.118	0.33	0.84		

According to Appendix B (equation 18), a computer program was used to determine the values of m and n that provided the best fit of the viscosity data at each temperature. The computer program is attached in Appendix C. The results are provided in Table 8-4 and Figures 8.6 and 8.7

Table 8-4 Power Law model constants(m , $s=1/n$)

Polymer/CO ₂ solution	M	S
5wt%	0.272	1.6
3wt%	0.026	1.2
1wt%	0.034	1.4
0.2wt%	0.003	1.1
0.1wt%	0.002	1.1

From Figure 8.6 , as copolymer concentration increase, the power law model constant s increases and $n=1/s$ decreases to values much less than 1(1 corresponds to a Newtonian fluid), the solution is more deviated from Newtonian fluid. From Fig. 8.7, as copolymer concentration increase, the power law model constant m increases with concentration, corresponding to the solution becoming more viscous.

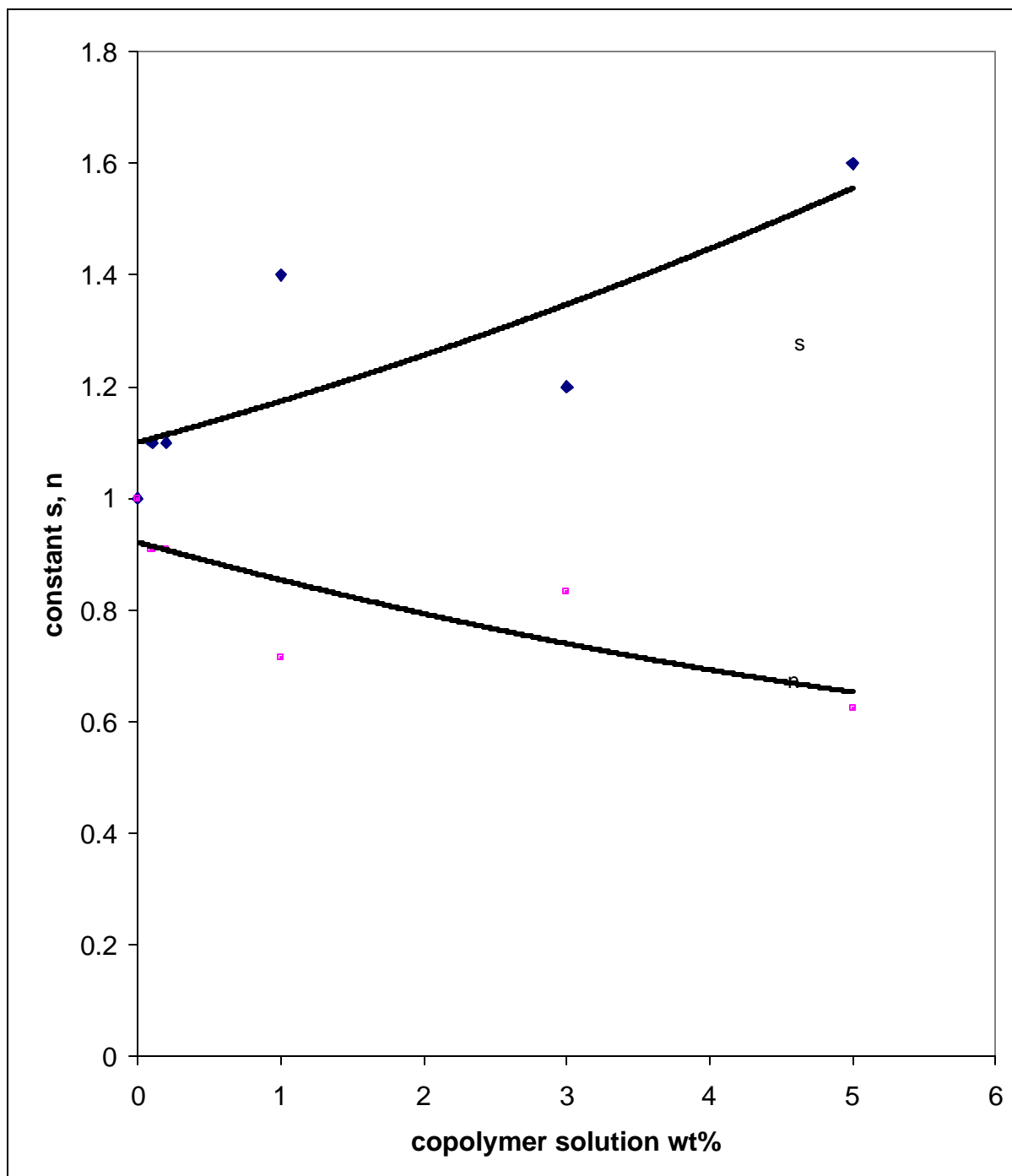


Figure 8.6 power law constant s , $n(=1/s)$ ($T=297\text{K}$, $P=34\text{MPa}$)

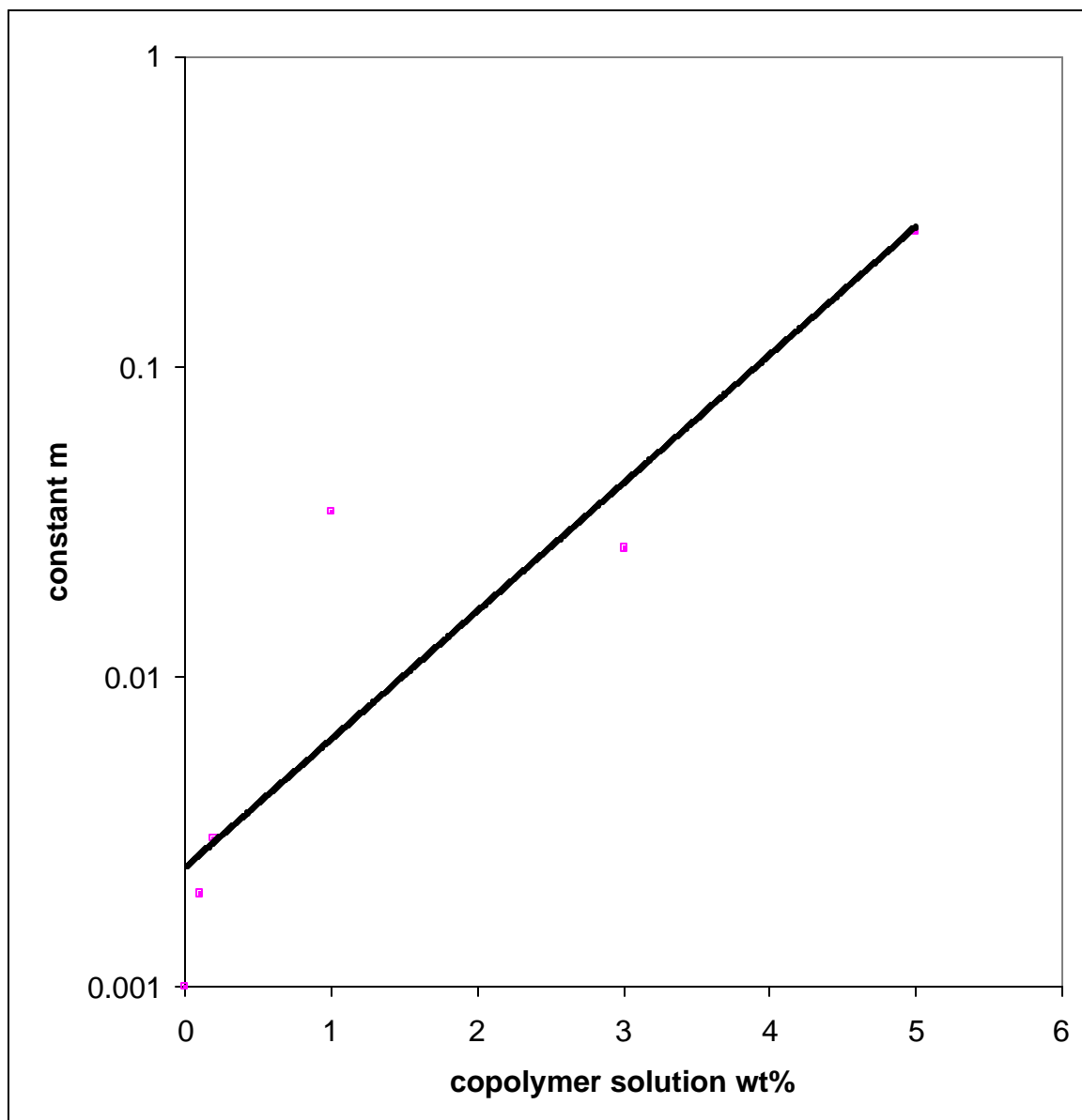


Figure 8.7 power law constant m ($T=297\text{K}$, $P=34\text{MPa}$)

Using the power model found in Appendix B, these results were illustrated in Fig 8.8. These results also indicate that the fluoroacrylate-styrene copolymer is an effective carbon dioxide thickener.

8.3 Flow-through-porous-media Viscometer Results

In order to simulate the field CO₂ flooding, we did experiment at superficial velocities of both 1 ft/day and 10ft/day flow rate. The permeability of the Berea sandstone cores was 80-200 md, as determined from experiments using neat carbon dioxide. The pressure drop was, as expected, much higher in 10 ft/day displacements. At the same flow rate, significantly higher pressure drops were detected for the fluoroacrylate-styrene copolymer/carbon dioxide solutions than for neat carbon dioxide.

The pressure drops along the core were on the order of 100-100000 Pa, depending on the superficial velocity and the copolymer concentration. This pressure drop was small relative to the pressure at the inlet face of the sandstone, which was maintained at 20MPa.

The pressure drops along each third of the core varied by no more than 5% for every mobility measurement. The variations were random, with no section of the core (particularly the inlet section) exhibiting a consistently greater pressure drop than the other sections. Therefore, no evidence of copolymer retention at the inlet face of the core was detected.

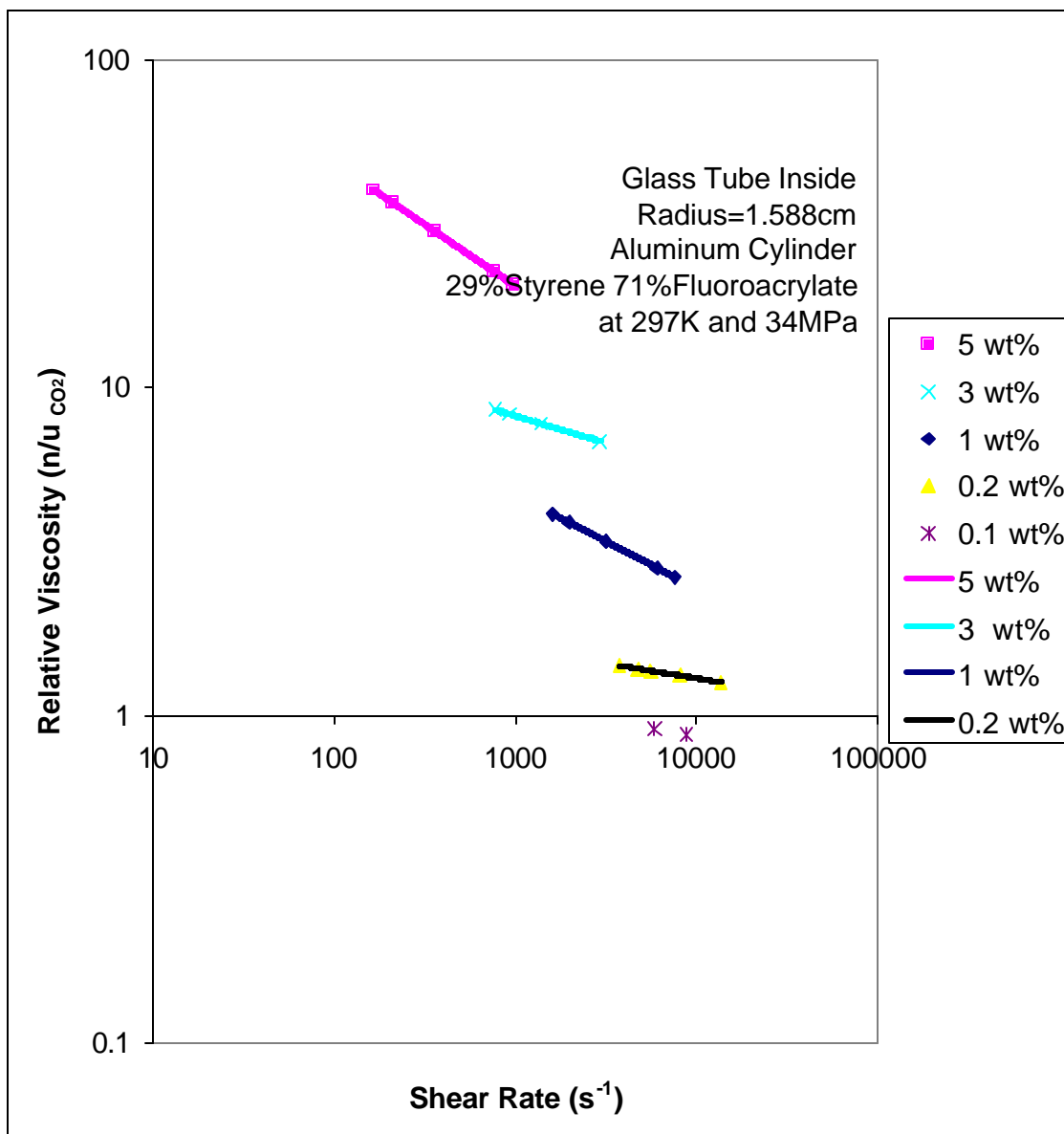


Figure 8.8 Relative Viscosity vs Shear Rate (Power Law)

Pressure drops of the neat and thickened carbon dioxide, flowing at the same superficial velocity, were used to estimate the increase in carbon dioxide viscosity. This viscosity increase at 298K and 20MPa is presented as a function of copolymer concentration for a constant superficial velocity, as illustrated in Table 8-5 and Figure 8.9. The pressure drops for both 1ft/day and 10ft/day are illustrated in Figure 8.10 and Figure 8.11.

The minimum concentration of thickener required to realize a significant increase in viscosity is about 0.5 wt%, while copolymer concentration as low as 0.25wt% were capable of thickening carbon dioxide. Significant increases in viscosity are attained as the concentration of the thickener increases to several weight percent. The 1.0wt% and 1.5wt% copolymer solution were 8 and 19 times more viscous than neat carbon dioxide, respectively, at a velocity of 0.00035cm/s (1 ft/day).

Because of the shear-thinning nature of the copolymer, increases in superficial velocity led to diminished thickening capability. For example, the addition of 1.5wt% copolymer increased the carbon dioxide viscosity by a factor of only 2 at a superficial velocity of 0.028cm/s (80 ft/day).

The permeability of the core to neat carbon dioxide that was injected after the copolymer solution agreed with the original measurement of permeability to within 1wt%. Therefore, the flow of the copolymer solution through the sandstone core did not result in any detectable permeability reduction.

These are the first measurements of a thickened carbon dioxide solution that requires no cosolvent and that elevates the viscosity of carbon dioxide by an order of magnitude at a concentration of only 1 wt%. This demonstrates that a carbon dioxide thickener can be developed if one designs the thickener specifically for dissolution in CO₂.

Table 8-5 Berea core flooding results

Flow rate	$\Delta P_{\text{solution}}/\Delta P_{\text{CO}_2}$					
	0wt%	0.2wt%	0.5wt%	1wt%	1.5wt%	2wt%
1ft/day	1	1.1	1.33	3.05	5.3	10.0
	1	1.05	1.38	2.96	5.1	11.0
	1	1.02	1.45	3.63	6.0	9.8
	1	1.04	1.61	3.61		
10ft/day	1	1.04	1.29	3.20	5.0	8.9
	1	1	1.27	2.82	5.0	8.8
	1			2.69	4.9	8.3
	1			2.82		

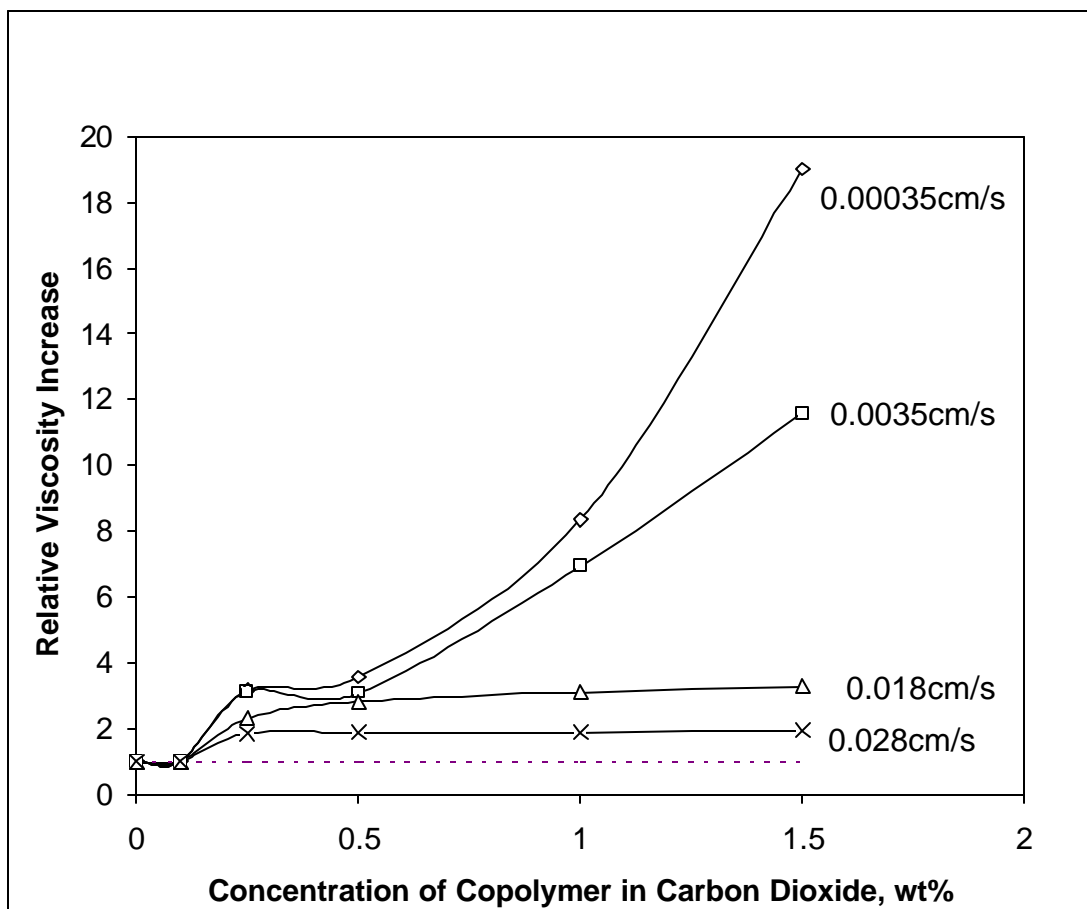


Figure 8.9 Relative viscosity increase vs. concentration at 298K, 20MPa, flowing through ~100md Berea sandstone

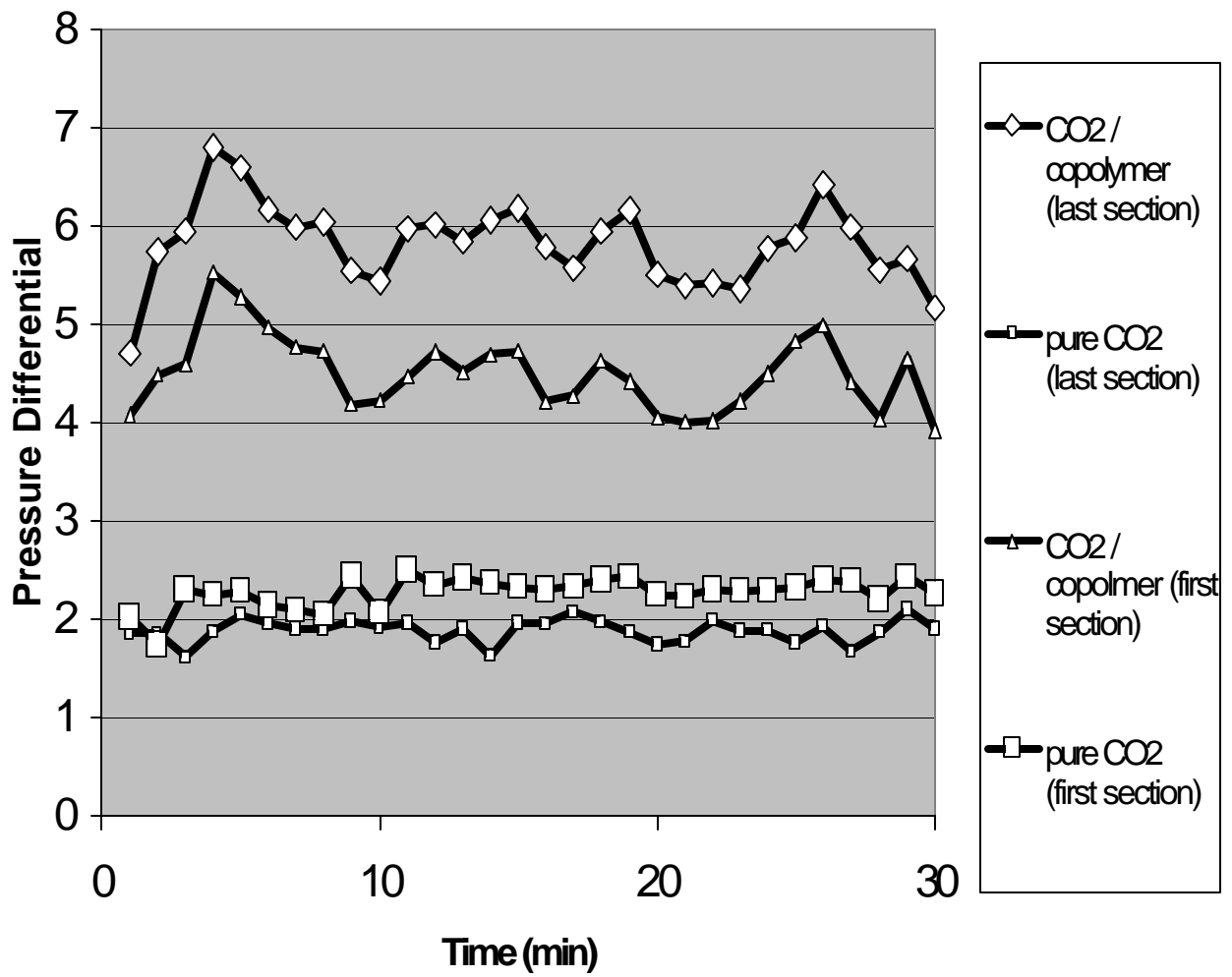


Figure 8.10 CO₂ flooding at 3500 psi and 1 ft/day

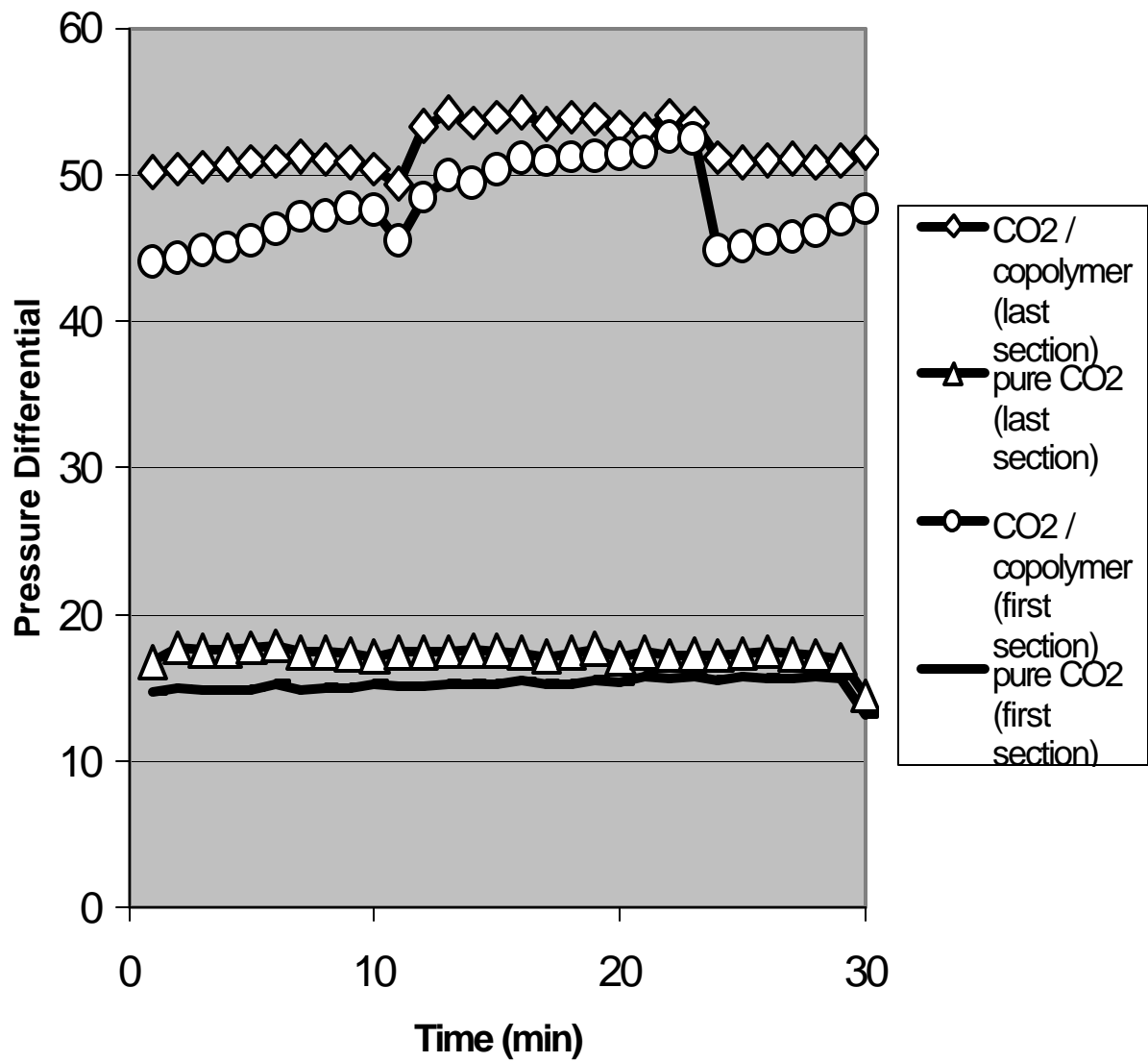


Figure 8.11 CO₂ flooding at 3500 psi and 10 ft/day

9.0 NON-FLUOROUS POLYMERS RESULTS

The fluoroacrylate-styrene copolymer is a *direct* thickener in that it does *not* require a cosolvent. Nonetheless, the fluoroacrylate-styrene copolymer is a highly fluorinated copolymer that is expensive, unavailable in large quantities and environmentally persistent. Rather than continuing to enhance the properties of fluoroacrylate-styrene copolymer (e.g. adjusting the composition and molecular weight (M_n) to attain higher solubility of fluoroacrylate-styrene copolymer at a specified pressure), a new generation of CO₂ thickeners has been designing at the University of Pittsburgh. Specifically, our current studies have been keeping focusing on inexpensive, biodegradable, *non-fluorous* direct thickeners that can be produced in large amounts and do *not* require an organic cosolvent to achieve dissolution. The same strategy used in the development of fluoroacrylate-styrene copolymer is being employed in the development of the non-fluorous thickener. Novel copolymers composed of carbon, hydrogen, oxygen and nitrogen has been designed to exhibit high CO₂ solubility. CO₂-phobic, associating groups will then be incorporated into the copolymer to impart thickening capabilities. The associating group content of the thickener composition will be adjusted to attain a reasonable balance of CO₂ solubility and thickening capability.

Non-fluorous thickening agents have not been identified yet. Work to date has being concentrated only on the identification of highly carbon dioxide-soluble, non-fluorous polymers. If such a polymer can be identified, it will then be modified to enhance its thickening capability. Some preliminary solubility results for the hydrocarbon-based polymers are presented below.

9.1 Polypropylene Oxide, PPO

From the literature, Propylene oxide homopolymer is the best non-fluorous homopolymer, the structure is shown in the figure 9.1. Monomer molecular formula:

$\text{OCH}(\text{CH}_3)\text{CH}_2$, monomer molecular weight: 58.82 g/mole

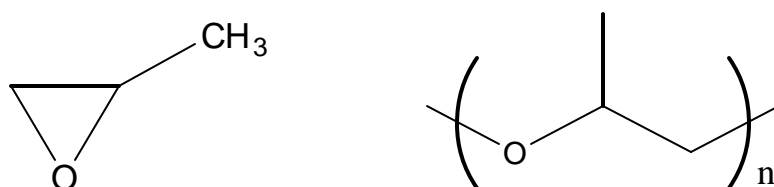


Figure 9.1 Propylene oxide monomer and homopolymer structure

Table 9-1 and Figure 9.9 shows that low molecular weight PPO ($M_w=2030$) was soluble in carbon dioxide at 298K, extremely soluble at low concentration. Our experiment result at 1wt% is in good agreement with previously reported solubility results at low concentration.^[27, 44] The cloud point pressure is strongly related to the polymer concentration at 298K. As the PPO concentration increased from 1 to 6 wt%, the cloud point pressure increased from 22MPa to 55MPa. However, higher molecular weight PPO can only dissolve in carbon dioxide at higher temperature, as shown at Figure 9.2. Although the upper critical solution temperature (UCST) behavior of the CO_2 -PPO ($M_w=3500$) system inhibited miscibility at temperature in 298-322K range; at the temperature range from 323K to 343K, the cloud point pressure decreases as the temperature increases.

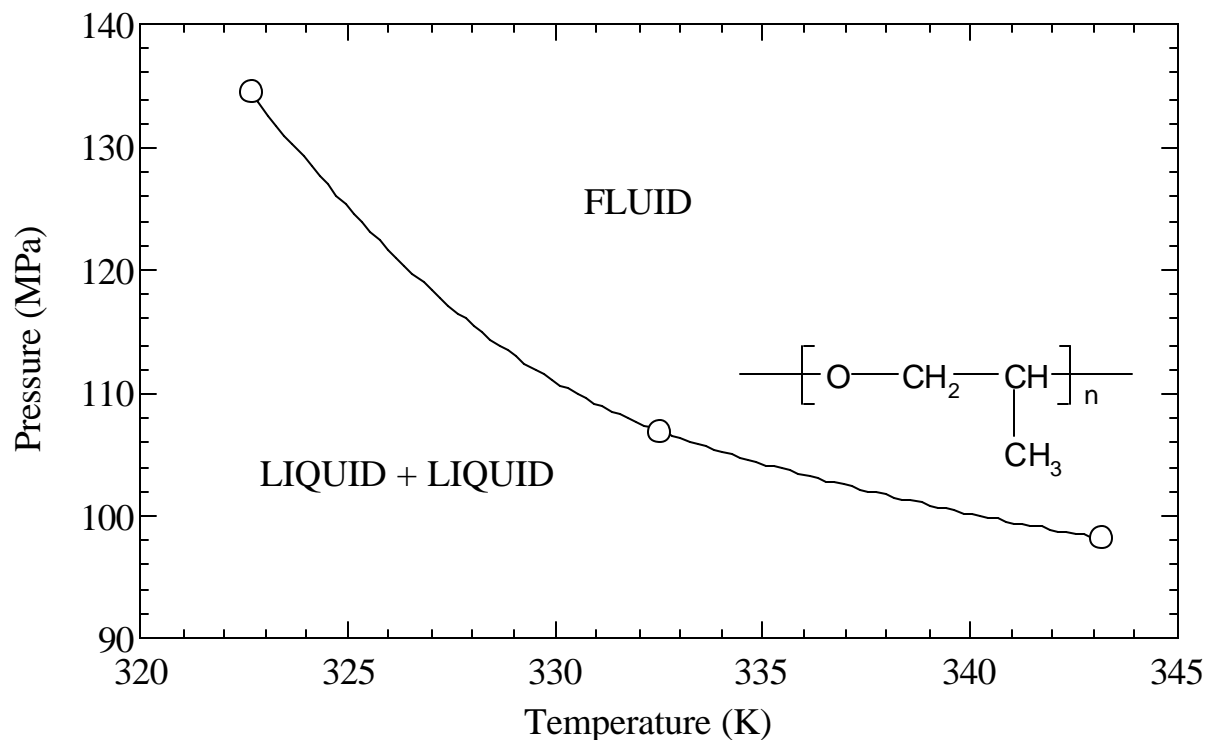


Figure 9.2 Cloud-point curve for ~5 wt% poly(propylene oxide) (PPO, $M_w = 3500$) – CO_2 mixture. Data from lab of Dr. Mark McHugh provided by Zhihao Shen of Virginia Commonwealth University.

9.2 Polybutadiene

The polybutadiene series polymers, including original polybutadiene from Aldrich ($M_n=1200$), polybutadiene with hydroxyl end and polybutadiene with acetate end, were not completely soluble in CO_2 at 7000psia and 1wt% concentration. The structure of the butadiene monomer and homopolymer, and acetate end-capped polybutadiene is shown in figure 9.3.

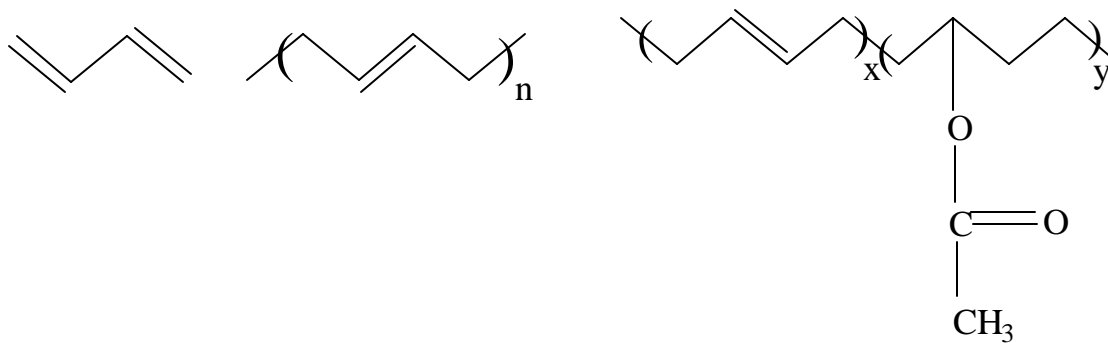


Figure 9.3 Butadiene monomer and homopolymer, and acetate end-capped poly BD

9.3 Polyethoxyethyl Acrylate

We investigated 2-Ethoxyethyl acrylate homopolymer (Mw: 11220, number average Mn: 8977, polydispersity index: 1.26), Figure 9.4. This polymer was CO₂ insoluble.

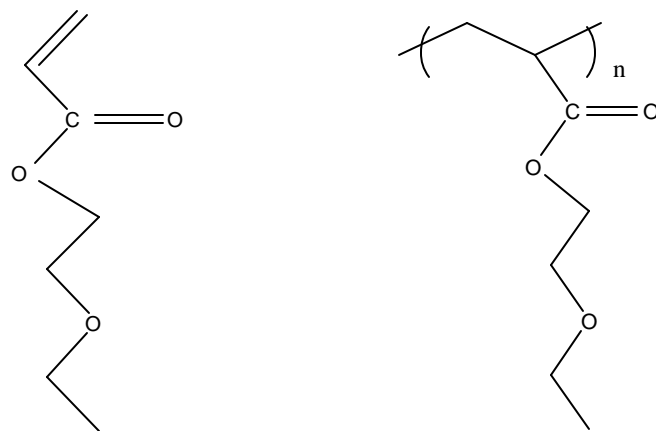


Figure 9.4 2-ethoxyethyl acrylate monomer and homopolymer

9.4 Polybutoxyethyl Acrylate

We investigated 2-butoxyethyl acrylate homopolymer (Mw: 8233, number average Mn: 6553, polydispersity index: 1.26), Figure 9.5. The polybutoxyethyl acrylate was CO₂ insoluble.

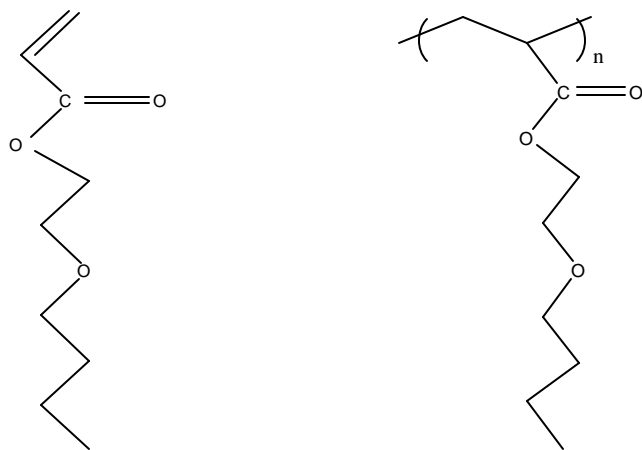


Figure 9.5 Butoxyethyl acrylate monomer and homopolymer

9.5 Polyvinyl Ester (VeoVa 10 Monomer)

We investigated the VeoVa 10, monomer, $R_1(C(R_2)(R_3))CO_2CH=CH_2$ where R_1 , R_2 , and R_3 are alkyl groups, at least one is a methyl, and the monomer molecular weight is 198 g/mole. The VeoVa 10 polymer (Mw: 16551, number average Mn: 10570, polydispersity index: 1.57), Figure 9.6, was CO₂ insoluble.

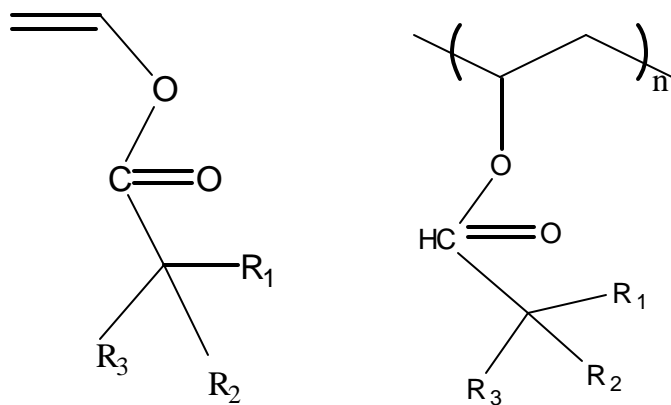


Figure 9.6 VeoVa 10 monomer and homopolymer

9.6 Poly Vinyl Acetate, PVAc

PVAc is the vinyl acetate homopolymer, the structure is shown in Figure 9.7. We synthesized several low molecular weight samples of PVAc and purchased from Aldrich. The GPC results are shown in Table 9-1.

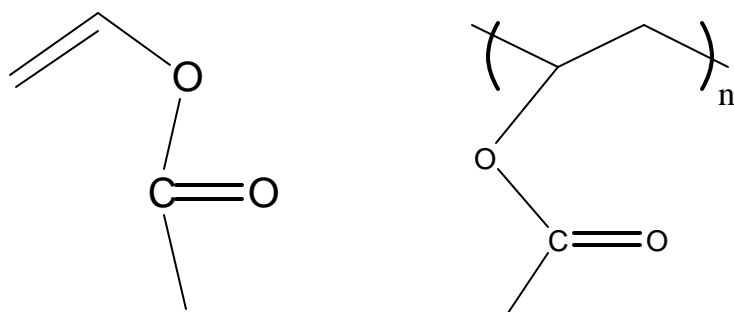


Figure 9.7 Vinyl acetate monomer and homopolymer structure

The very low PVAc solubility data proved to be comparable to that of polypropylene oxide, although the PVAc-CO₂ Px profiles were much flatter than the PPO-CO₂ profiles. We

synthesized poly vinyl acetate using atom transfer radical polymerization in order to control molecular weight. The extremely high cloud point pressures for some PVAc were obtained with the help of Dr. Mark McHugh and Dr. Zhihao Shen of Virginia Commonwealth University. The solubility results are shown in Figure 9.8 and Figure 9.9.

The CO₂ solubility of polyvinyl acetate is quite promising. Polyvinyl acetate does dissolve in CO₂ in large amounts. The solubility curves for PVAc were fairly flat over a wide range of concentration, for all the different MW samples we investigated. We also found that as molecular weight increase, the pressure required to dissolve PVAc in carbon dioxide increase, which is shown as expected. The results, figure 9.9, shows that the cloud point pressure, for the two lowest molecular weight PVAc (PVA2063 and PVAc3092), are very close, almost identical, because the lower Mn one has higher dispersity index PDI 2.01, much higher than that of the higher Mn PVAc, which is 1.5. The broader distribution of polymers causes the high apparent cloud point pressure.

PVAc and PPO of comparable repeat units have similar solubility at 3wt%. Above 3wt%, PVAc is more soluble than PPO, while below 3wt%, PPO is more soluble. Unlike PVAc, PPO is very sensitive to the sample concentration in carbon dioxide. As concentration increases, the pressure needed to dissolve PPO in carbon dioxide increases dramatically. And at the concentration of 6wt%, PPO solubility test is above the range of our Ronbinson Cell capacity.

However, PVAc was not as CO₂-soluble as polyfluoroacrylate or the fluoroacrylate-styrene copolymer thickener, as shown in Figure 8-2. These fluoropolymers were soluble in carbon dioxide at much lower pressures than that of PMA, PPO and PVAc. For example, the fluoroacrylate-styrene copolymer (Mn=539600), with 867 repeat units, is more soluble than PVAc (Mn=3092), with 36 repeat units.

Figure 9.9 shows that compared with the phase behavior of molecular weight 2300 PPO, two phase locus of PVAc-CO₂ mixtures exhibits a relatively flat profile over the 1~12 wt% region at 298K with the cloud point pressure maximum occurring near 5wt% concentration. The cloud point pressure increases with PVAc chain length.

For even longer PVAc, the highest molecular weight PVAc (Mw=500000) in our experiment, is still soluble in carbon dioxide at 298K at a pressure of 68MPa. The temperature – cloud point pressure relationship is illustrated in figure 9.8, for two high molecular weight PVAc samples (Mw=125000 and Mw=585000). The strength of the CO₂-acetate interaction is apparently great enough to overcome repeat group-repeat group interactions, and entropic effects associated with polymer conformation do not have a dramatic effect on the cloud point pressure. From Figure 9.8 and Figure 9.9, higher molecular weight PVAc need higher pressure to get dissolved in carbon dioxide.

In Figure 9.9, we also compared the cloud point pressure of poly propylene oxide (PPO), poly vinyl acetate (PVAc), and poly methyl acetate (PMA), the molecular weight is also listed in the figure 9.9. More physical property information is available in Table 9.1.

Although PVAc is a promising non-fluorous, carbon dioxide soluble homopolymer, it is far less CO₂-philic than fluoroalkyl acrylate polymers (PFA). PFA typically has a linear side-chain terminated with a long fluorocarbon segment, such as poly(heptadecafluorodecyl acrylate).

DeSimone pioneered the incorporation of fluoroalkyl acrylate into a homopolymer or copolymer to attain carbon dioxide solubility.^[45] Figure 9.12 illustrates that the cloud point pressure of PFA are significantly lower than those of PVAc.^[46-48] This difference is contributed to CO₂-phobic attribute of PVAc relative to PFA at low pressures, which has been used to facilitate the emulsion polymerization of vinyl acetate in carbon dioxide.^[49]

Despite having identified PVAc as the most CO₂ soluble, non-fluorous, commercial polymer, the pressure required to dissolve high molecular weight PVAc is much greater than the MMP of CO₂ floods. Therefore, PVAc is *not* CO₂-philic enough to serve as the polymeric basis of non-fluorous CO₂ thickeners.

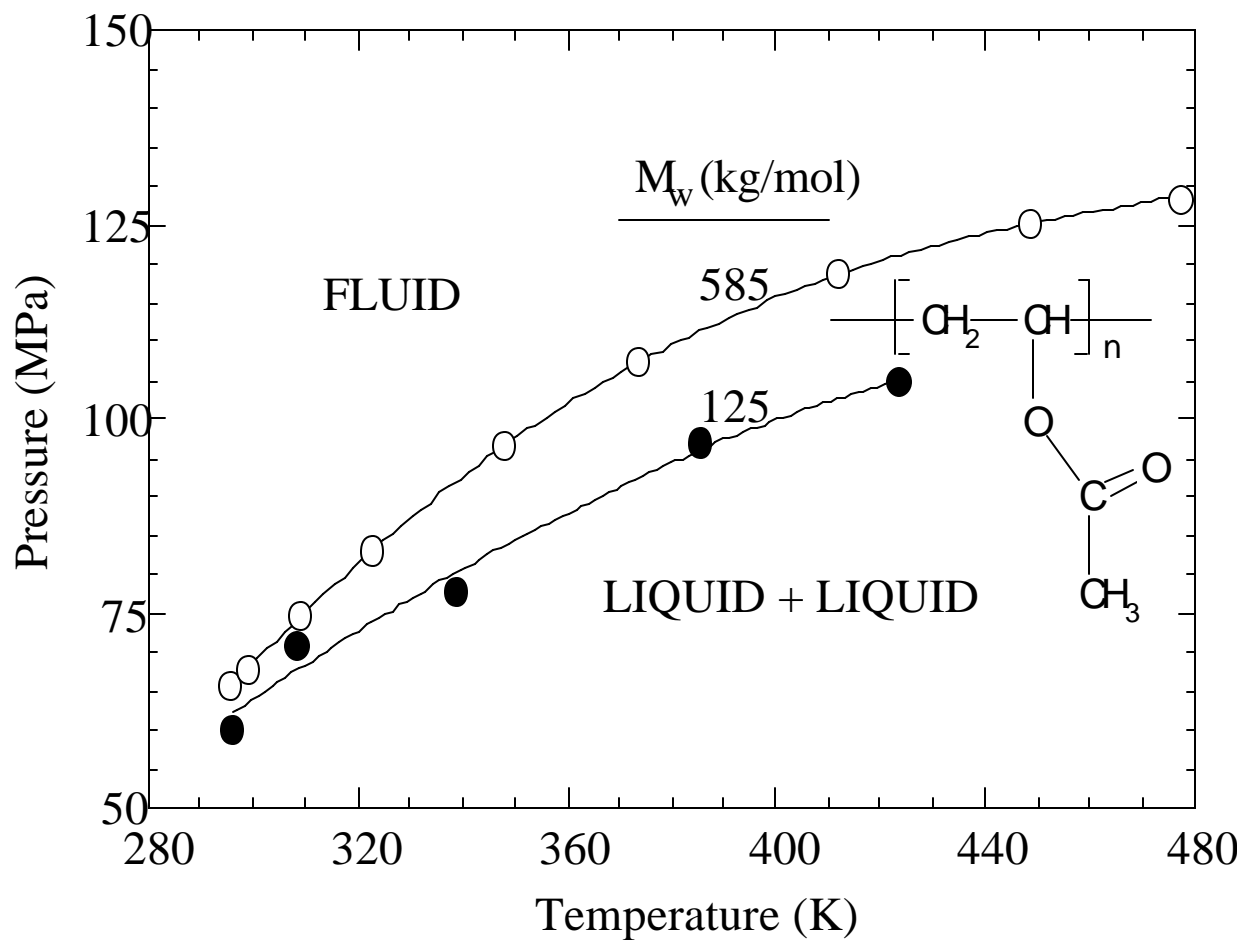


Figure 9.8 Effect of polymer molecular weight on the cloud-point curves for ~5 wt% poly(vinyl acetate) (PVAc) – CO₂ mixtures. (Filled circles – data from Rindfleisch, et al. 1996; open circles – data from our experiments.)

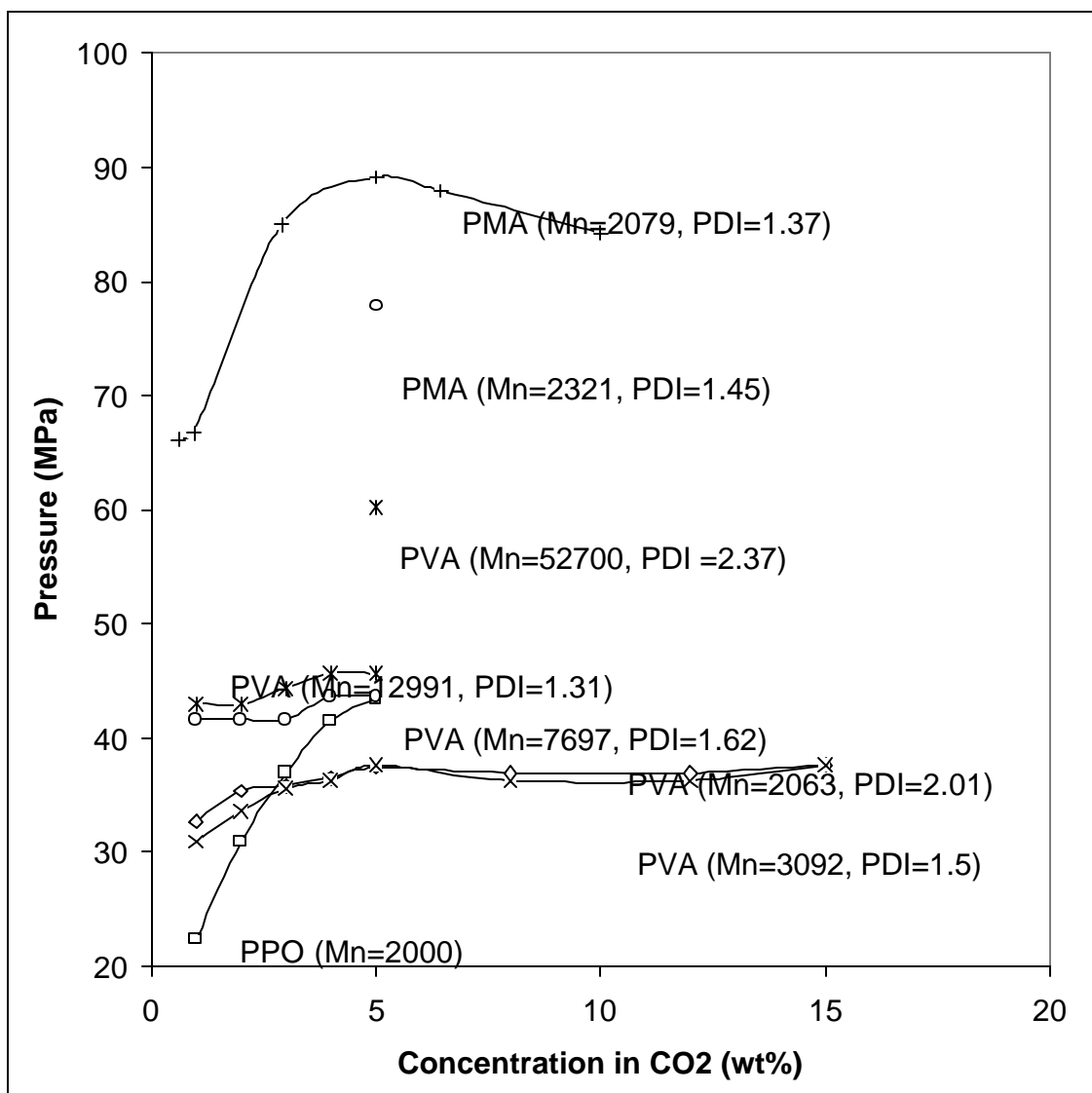


Figure 9.9 Phase behavior of PVA, PPO and PMA at 298K

9.7 Poly Methyl Acrylate, PMA

PMA is identical to PVAc except that the position of the carbonyl is switched. To make a valid comparison, short polymers or oligimers of PPO, PVAc and PMA were employed. Samples of PMA and PVAc with comparable molecular weight or number of repeat units relative to PPO 2000 were prepared. Monomer molecular formula: $\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3$, monomer molecular weight: 86.09, compound structure is shown in Figure 9.10.



Figure 9.10 Methyl acrylate monomer and homopolymer

To make the comparison more meaningful, we compared PPO, PVAc and PMA with the same number of repeat unit or same molecular weight, corresponding to PPO 2000. With the small difference in the structure between PMA and PVAc, a big solubility difference was exhibited. We cannot dissolve the PMA in our Ronbinson Cell, Dr. Mark McHugh at Virginia Commonwealth University helped us get the extremely high cloud point pressures. The pressure required to dissolve the higher molecular weight PMA ($M_n=2321$) is slightly less than that required for the lower molecular weight sample ($M_n=2079$). We attribute this unusual trend to

residual amounts of co-solvent that were left in the PMA 2321 sample, because the PMA 2321 was less viscous than, not more viscous as it was supposed to, the PMA 2079. The solubility results are shown in Figure 9-10.

From the solubility data of PMA and PMAc, it is quite interesting to know why a little change in the structure causes such a big solubility difference. It is expected the relative position of carbonyl group and backbone carbon chains play an important role here, as well as the ether oxygen. The real atom and molecular correlation, and pros and cons for the carbon dioxide solubility are still under investigation, with the help of Dr. Johnson of Chemical and Petroleum Engineering Department at the University of Pittsburgh.

With the help from Dr. Mark McHugh at Virginia Commonwealth University, we also investigated the temperature effect on the PMA carbon dioxide solubility. From Figure 9-11, at temperature range between 25-50°C, at low concentration, as the PMA concentration increase, the required pressure to dissolve PMA also increases; while at higher concentration (>5wt%), the concentration doesn't have a big effect on the required pressure. The PMA isotherms exhibit a maximum value at about 5wt% PMA at each temperature, which has been previously observed by other polymer-solvent mixtures. [25, 50-54]

PMA is much less soluble in carbon dioxide than PVAc even though the repeat group of both polymers is slightly rearranged. Figure 9.12 illustrates that the cloud point pressure of PMA increases dramatically as the molecular weight increases, while cloud point pressure of PVAc increases much slower than that of PMA. Because PMA carbonyl group is closer to the polymer backbone, which can not move freely; on the other hand, the PVAc carbonyl group can rotate freely due to the ether linkage between the polymer backbone and the acetate.

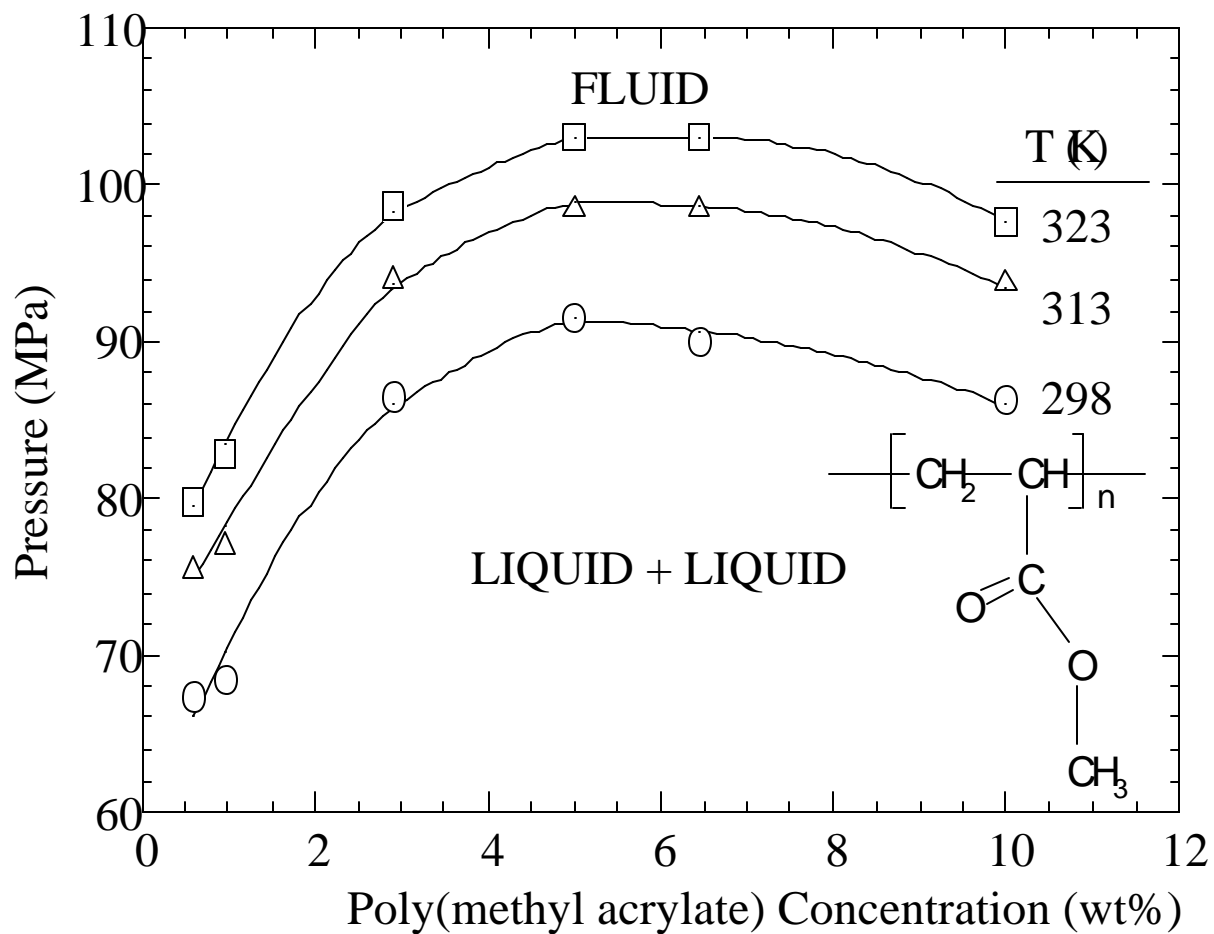


Figure 9.11 Pressure-composition isotherms for the system CO₂ – poly(methyl acrylate) (PMA) ($M_w = 2850$) at 298, 313, and 323 K. High pressure data (>70MPa) provided by Mark McHugh and Zhihao Shen of Virginia Commonwealth University.

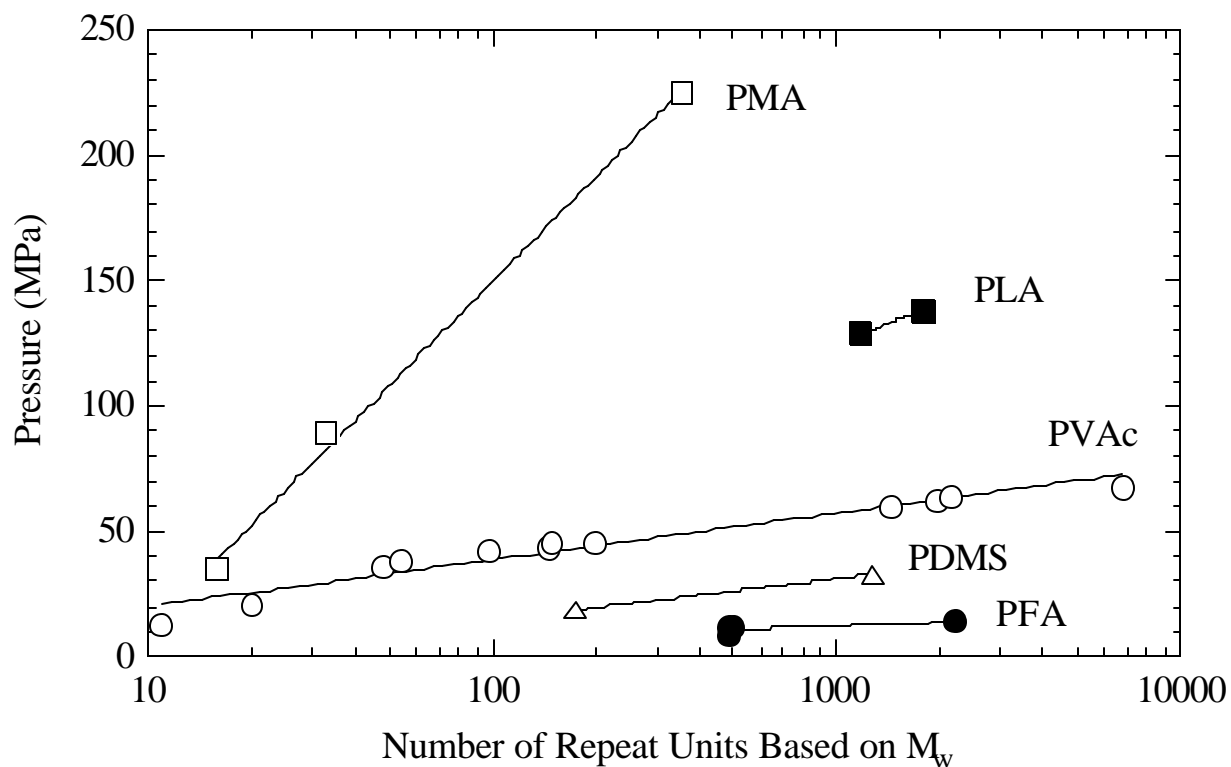


Figure 9.12 Cloud-point pressures at ~5 wt% polymer concentration and 298 K for binary mixtures of CO₂ with poly(methyl acrylate) (PMA), poly(lactide) (PLA), poly(vinyl acetate) (PVAc), poly(dimethyl siloxane) (PDMS), and poly(fluoroalkyl acrylate) (PFA) as a function of number of repeat units based on M_w . High pressure data (>70MPa) provided by Mark McHugh and Zhihao Shen of Virginia Commonwealth University.

9.8 Poly Vinyl Formate, PVF

Encouraged by the promising result of PVAc, we investigated poly vinyl formate (Mw: 2327, number average Mn: 1068, polydispersity index: 2.18), Figure 9.13, which is identical in structure to poly vinyl acetate except that the methyl of the acetate is replaced by hydrogen. Recently, Scott Wallen and coworkers have indicated that a cooperative weak hydrogen bond may occur between the oxygen of CO₂ and the terminal hydrogen of the formate monomer. This interaction may lead to enhanced carbon dioxide solubility of poly vinyl formate.^[55]

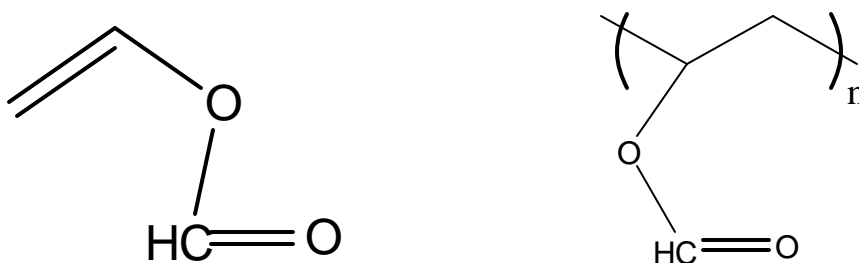


Figure 9.13 Vinyl formate monomer and homopolymer

Poly vinyl formate is cannot dissolve in carbon dioxide. This result is consist with the previous observations,^[25,56] which concluded that very polar or hydrogen bonded polymers do not dissolve in carbon dioxide. Vinyl formate will interact with itself more strongly than that of acetate, even though the formate proton is not highly acidic. Nonetheless, this interaction with itself is much stronger than the CO₂-formate interaction, causing PVF to be carbon dioxide insoluble.

9.9 Methyl Isobutyrate (MIB) and Isopropyl Acetate (IPA)

The carbon dioxide solubility difference between methyl acrylate and vinyl acetate is so significant, with a little difference in their structure. We decided to study methyl isobutyrate and isopropyl acetate. These compounds serve as models of the repeat unit of PMA and PVAc, respectively. They both have the same molecule composition, have molecular formulas: $(\text{CH}_3)_2\text{CHCO}_2\text{CH}_3$ and $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)_2$, respectively. We tried to investigate the effect of the structure difference on small molecular. The structures of the MIB and IPA are shown in Figure 9.14.

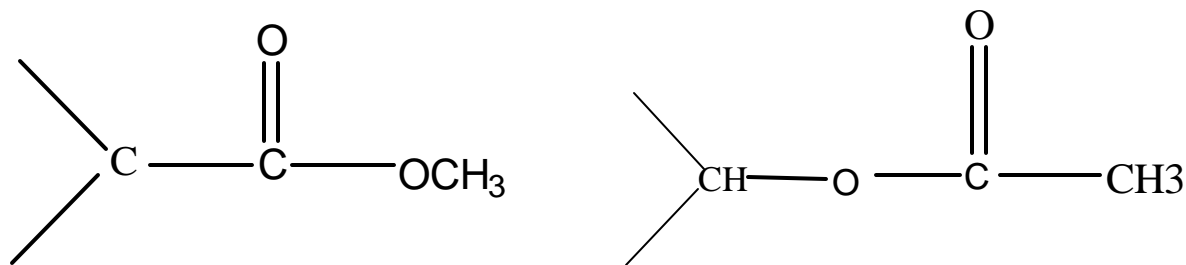


Figure 9.14 methyl isobutyrate and isopropyl acetate

MIB and IPA have the same molecular formula, with the small dislocation of the atoms in the structure. They have the similar carbon dioxide solubility. The solubility results of MIB and IPA are shown in Figure 9.15. So, the solubility results from MIB and IPA proved that the structure dislocation doesn't have effect on small molecules. From Figure 9.12, the dislocation of the carbonyl group with the molecules has no effect in solubility in small molecules, while there is a significant effect on the solubility in polymers.

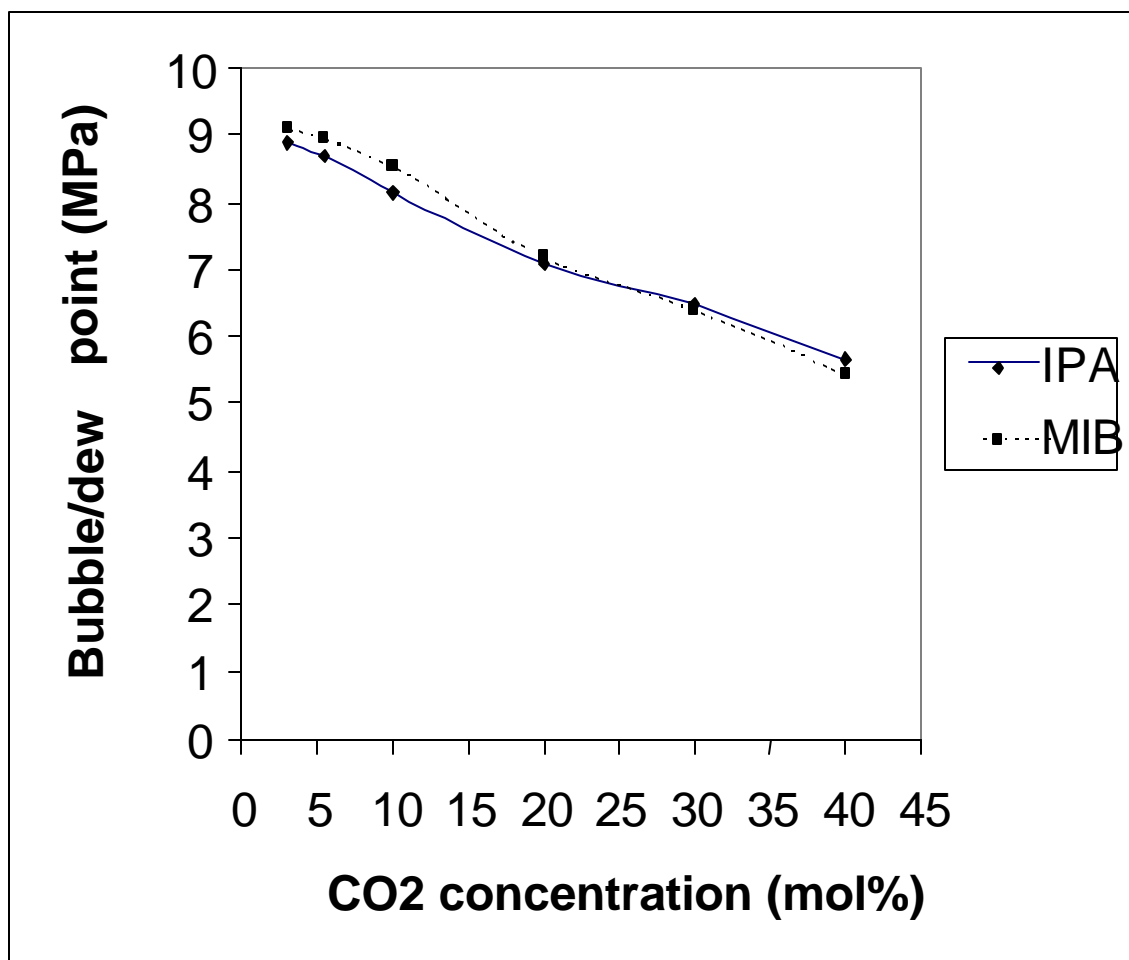


Figure 9.15 Phase Behavior of Methyl Isobutyrate and Isopropyl acetate in CO₂ (T=323K), critical point in the 3-5wt% range

9.10 Poly Dimethyl Siloxane

The solubility of polydimethylsiloxane in carbon dioxide has been previously reported at 298K.^[27,57] Silicone homopolymers are also more carbon dioxide soluble than PVAc as seen in Figure 9.12, although PDMS is not as carbon dioxide soluble as PFA. The structure of PDMS is shown in Figure 9.16.

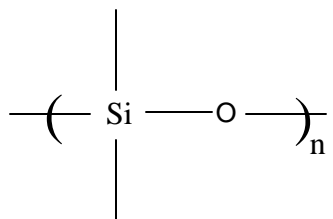


Figure 9.16 Poly (dimethyl siloxane) structure

Table 9-1 Molecular weight of PMA, PVAc, PPO and PVF*.

Polymer	M_n	M_w	M_w/M_n	$N_{RU,n}$	$N_{RU,w}$	P_{cp} (MPa)
PMA	780	1390	1.78	9	16	34.6
	2080	2850	1.37	24	33	89.1
	10600	30700	2.90	123	357	225.0 ^a
PVAc	780	980	1.25	9	11	13.6
	850	1700	2.00	10	20	20.8
	2060	4150	2.01	24	48	37.4
	3090	4640	1.5	36	54	37.6
	5680	8380	1.47	66	97	42.0
	7700	12500	1.62	89	145	43.6
		12800			149	45.7
	13000	17000	1.31	151	198	45.7
	52700	124800	2.37	612	1451	60.2 ^a
		167000			1941	62.5
	61600	182000	2.95	716	2116	63.7
	193000	585000	3.02	2244	6802	67.6
PPO	1640	2030	1.24	28	35	43.6
		3500			60	Insoluble
PVF	1070	2327	2.18	15	27	Insoluble

^a Data from Rindfleisch, et al. 1996.

* This table includes number averaged molecular weight (M_n), weight averaged molecular weight (M_w), polydispersity (M_w/M_n), number of repeat units based on M_n ($N_{RU,n}$), and number of repeat units based on M_w ($N_{RU,w}$), for poly(methyl acrylate) (PMA), poly(vinyl acetate) (PVAc), poly(propylene oxide) (PPO), and poly(vinyl formate) (PVF) and cloud-point pressures (P_{cp}) for their binary mixtures with CO₂ at ~5 wt% and 298 K.

10.0 CONCLUSION AND FUTURE WORK

1. We have successfully identified the first CO₂ thickener, the fluoroacrylate-styrene random copolymer (71mol% fluoroacrylate-29mol% styrene) synthesized via bulk, free-radical polymerization. This copolymer has a number-average molecular weight of 540,000 and a polydispersity index of 1.63. The fluoroacrylate-styrene copolymer exhibited remarkably high solubility in dense carbon dioxide, which was attributed to the high fluoroacrylate content of the copolymer.
2. The thickening capability of fluoroacrylate-styrene copolymer over the 298 – 373 K temperature range was attributed to intermolecular **p-p** stacking of the aromatic rings associated with the styrene monomer. Previous research demonstrated that fluoroacrylate copolymers lacking the pendent phenyl group did not thicken CO₂.
3. Pressure drop measurements of the fluoroacrylate-styrene copolymer-carbon dioxide solutions flowing through Berea sandstone demonstrated that the fluoroacrylate-styrene copolymer could effectively reduce the mobility of carbon dioxide at superficial velocities up to 0.0035cm/s (10ft/day). Higher velocities and lower copolymer concentration resulted in much smaller reductions in mobility. For example, the apparent viscosity of carbon dioxide was increased by a factor of 7-8 at superficial velocities of 0.00035-0.0035cm/s (1-10ft/day) for a 1wt% solution of the copolymer in carbon dioxide, and the apparent viscosity of carbon dioxide was increased by a factor of 12-19 at the same velocities range for 1.5wt% solution.
4. The fluoroacrylate-styrene copolymer-carbon dioxide solution illustrated shear-thinning behavior. As the shear rate increases, the viscosity of the solution decreases.

5. Poly vinyl acetate is the most promising non-fluorous base polymer, composed of carbon, hydrogen and oxygen, identified up to date. The high solubility is reflected by the relatively low pressure required to attain dissolution of approximately 5wt% polymer at 298K. Unfortunately, the pressure required to dissolve PVAc in CO₂ greatly exceed the MMP of CO₂ floods. Therefore, PVAc is not CO₂-philic enough to be used in the design of CO₂ thickeners.
6. Other carbonyl-rich polymers, including PMA, containing similar functional groups were significantly less soluble or insoluble in carbon dioxide due to their crystallinity, lack of side chains, or less accessible to carbonyl groups.
7. Less expensive CO₂-philic functional groups are to be developed to replace the more expensive fluororous CO₂-philic functionalities in the thickener structures. Ideally, hydrocarbon based structures, which is bio-degradable, are to be incorporated into the CO₂ thickener structures, to make it environmentally benign, as well as economically possible.
8. We will continue designing our non-fluorous base polymers, and find a better base polymer more CO₂ soluble than PVAc, hopefully the new hydrocarbon-based non-fluorous base polymer can match the solubility of the fluoroacrylate-base polymers. After that, we will incorporate CO₂-phobic, interacting groups into the polymer in order to greatly increase the CO₂ solution viscosity.

APPENDICES

APPENDIX A

NEWTONIAN FLUID MODEL DEVELOPMENT

1. Start from Navier-Stokes equation:

For a control volume unit in the annular gap,

$$r\left(\frac{\partial V_z}{\partial t} + V_r \frac{\partial V_z}{\partial r} + V_\theta \frac{\partial V_z}{\partial \theta} + V_z \frac{\partial V_z}{\partial z}\right) = -\frac{dp}{dz} + \mu \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V_z}{\partial r} \right) + \frac{1}{r^2} \left(\frac{\partial^2 V_z}{\partial \theta^2} \right) + \frac{\partial^2 V_z}{\partial z^2} \right) + rgz \quad (1)$$

2. Simplify equation (1),

$$\frac{dp}{dz} = \mu \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V_z}{\partial r} \right) \right) \quad (2)$$

because all the other terms are zero, so

$$\frac{1}{\mu} \frac{dp}{dz} = \frac{1}{r} \left(r \frac{\partial^2 V_z}{\partial r^2} + \frac{\partial V_z}{\partial r} \right)$$

$$\frac{1}{\mu} \frac{dp}{dz} = \frac{\partial^2 V_z}{\partial r^2} + \frac{1}{r} \frac{\partial V_z}{\partial r}$$

3. The solution to this 2nd order differential equation is:

$$V_z = \frac{1}{4\mu} \frac{dp}{dz} r^2 + C \ln r + B \quad (3)$$

4. Boundary Conditions:

$$V_z = 0, \quad @ r = r_t \quad (4)$$

$$V_z = V_c \quad @ r = r_c \quad (5)$$

5 with these boundary conditions, we can get the constants in equation (3)

$$B = -\frac{1}{4\mathbf{m}} \frac{dp}{dz} r_t^2 - C \ln r_t \quad (6)$$

$$C = \frac{V_c + \frac{1}{4\mathbf{m}} \frac{dp}{dz} (r_t^2 - r_c^2)}{\ln\left(\frac{r_c}{r_t}\right)} \quad (7)$$

6, Substitute (6), (7) into equation (3),

$$V_z = \left(V_c + \frac{1}{4\mathbf{m}} \frac{dp}{dz} (r_t^2 - r_c^2) \right) \frac{\ln\left(\frac{r}{r_t}\right)}{\ln\left(\frac{r_c}{r_t}\right)} - \frac{1}{4\mathbf{m}} \frac{dp}{dz} (r_t^2 - r^2) \quad (8)$$

7. Now, according to the total liquid volume are constant, so the liquid is displaced is equal to the liquid flowing through the annular gap.

$$-p r_c^2 V_c = 2p \int_{r_c}^{r_t} V_z(r) r dr \quad (9)$$

8. Substitute equation (8), V_z into (9), and simplify,

$$\frac{dp}{dz} = - \frac{4\mu V_c}{(r_t^2 - r_c^2) + \ln \frac{r_c}{r_t} (r_t^2 + r_c^2)} \quad (10)$$

9. Now substitute equation (10), dp/dz into equation (8),

$$V_z = V_c \cdot \left[\frac{(r_t^2 - r_c^2) - \frac{\ln(r/r_t)}{\ln(r_c/r_t)} (r_t^2 - r_c^2)}{(r_t^2 - r_c^2) + \ln(r_c/r_t) (r_t^2 + r_c^2)} + \frac{\ln(r/r_t)}{\ln(r_c/r_t)} \right] \quad (11)$$

10. According to Newton's 2nd Law, when terminal velocity is reached, $dv_z/dt=0$, the piston is in force balance:

$$G = F_1 + F_2 + F_3 \quad (12)$$

here, G is gravity,

$$G = p r_c^2 l r_c g \quad (13)$$

F_1 is the force on the piston vertical surface,

$$F_1 = s \times t = -2p r_c l m \left(\frac{\eta V_z}{\eta r} \right) \Bigg|_{r=r_c} \quad (14)$$

F₂ is the force on the piston top and bottom surface because of pressure difference,

$$F_2 = p r_c^2 l \frac{dP}{dZ} \quad (15)$$

F₃ is the force because of buoyancy,

$$F_3 = p r_c^2 l r_f g \quad (16)$$

Substitute G, F₁, F₂, F₃ into equation (12),

$$p r_c^2 l (r_c - r_f) g = -2p r_c l m \left(\frac{\eta V_z}{\eta r} \right) \Bigg|_{r=r_c} + p r_c^2 l \frac{dP}{dZ} \quad (17)$$

11, From equation (11), differentiate V_z with r, so, Shear Rate, dv_z/dr,

$$\frac{\eta V_z}{\eta r} = \frac{dV_z}{dr} = V_c \cdot \left[\frac{-2r - (r_t^2 - r^2) \frac{1}{r \ln(r/r_t)}}{(r_t^2 - r^2) + \ln(r/r_t)(r_t^2 + r^2)} + \frac{1}{r \ln(r/r_t)} \right]$$

Notice $r=r_c$, at the piston vertical surface

$$\left. \frac{V_z}{r} \right|_{r=r_c} = \left. \frac{dV_z}{dr} \right|_{r=r_c} = V_c \cdot \left[\frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{(r_t^2 - r_c^2) + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \right] \quad (18)$$

$$\left. \frac{V_z}{r} \right|_{r=r_c} = \left. \frac{dV_z}{dr} \right|_{r=r_c} = V_c \cdot K' \quad (19)$$

and

$$K' = \frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{(r_t^2 - r_c^2) + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \quad (20)$$

12, Also, from equation (10),

$$\frac{dp}{dz} = J' \cdot \mathbf{m} V_c \quad (21)$$

and

$$J' = - \frac{4}{(r_t^2 - r_c^2) + \ln \frac{r_c}{r_t} (r_t^2 + r_c^2)} \quad (22)$$

13. Now, substitute equation (19), (21) into equation (17), and simplify,

$$\mathbf{m} = \frac{r_c (\mathbf{r}_c - \mathbf{r}_f) g}{V_c (r_c J' - 2K')} \quad (23)$$

14, We assume fluid is Newtonian fluid,

$$\mathbf{m} = K \frac{\mathbf{r}_c - \mathbf{r}_f}{V_c} \quad (24)$$

or ,

$$V_c = K \frac{\mathbf{r}_c - \mathbf{r}_f}{\mathbf{m}} \quad (25)$$

and

$$K = \frac{r_c g}{r_c J' - 2K'} \quad (26)$$

15, For relative viscosity, according to equation (24), we can get it from the ratio of terminal velocity of sample solution to that of pure CO₂

$$Relative\ Viscosity = \frac{\mathbf{m}_{sample}}{\mathbf{m}_{co2}} = \frac{V_{c_{co2}}}{V_{c_{sample}}} \quad (27)$$

16, For clearness, write the Shear Rate again, from equation (18),

$$Shear\ Rate = \frac{dV_z}{dr} = Vc. \left[\frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{(r_t^2 - r_c^2) + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \right] \quad (28)$$

Example:

At 34Mpa (5000psi), 297K,

Pure CO₂, viscosity $\mu_{CO_2}=1181.7\mu P$, density $\rho_f=0.9888g/cc$

Falling cylinder, Aluminum density $\rho_c=2.7g/cc$

Sample: 5wt% Copolymer (29%Styrene71%Fluoroacrylate)

Diameter of Glass Tube: 1.2500" (D_t)

Diameter of Piston: 1.2399" (D_c)

Terminal velocity of pure CO₂: $V_{c_{sample}}=0.471cm/s$

Terminal velocity of sample: $V_{c_{CO_2}}=0.004945cm/s$

First, calculate r_t , and r_c

$$r_t = D_t/2 = 1.2500inch * (2.54cm/inch) / 2 = 1.5875cm$$

$$r_c = D_c/2 = 1.2399inch * (2.54cm/inch) / 2 = 1.5747cm$$

So, from equation (27),

$$Relative\ Viscosity = \frac{\mu_{sample}}{\mu_{CO_2}} = \frac{V_{c_{CO_2}}}{V_{c_{sample}}} = \frac{0.471cm/s}{0.004945cm/s} = 95.25$$

From equation (20),

$$\begin{aligned}
 K' &= \frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{r_t^2 - r_c^2 + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \\
 &= \frac{-2 \times 15747 - (15875^2 - 15747^2) \frac{1}{15747 \ln(15747 / 15875)}}{(15875^2 - 15747^2) + \ln(15747 / 15875)(15875^2 + 15747^2)} + \frac{1}{15747 \ln(15747 / 15875)} \\
 &= -29068 \text{ cm}^{-1}
 \end{aligned}$$

From equation (22),

$$\begin{aligned}
 J' &= - \frac{4}{(r_t^2 - r_c^2) + \ln \frac{r_c}{r_t} (r_t^2 + r_c^2)} \\
 &= - \frac{4}{(15875^2 - 15747^2) + \ln(15747 / 15875)(15875^2 + 15747^2)} \\
 &= 4523534 \text{ cm}^{-2}
 \end{aligned}$$

From equation (26),

$$\begin{aligned}
 K &= \frac{r_c g}{r_c J' - 2K'} \\
 &= \frac{15747 \text{ cm} \times 980 (\text{cm} / \text{s}^2)}{15747 \text{ cm} \times 4523534 \text{ cm}^{-2} - 2 \times (-29068) \text{ cm}^{-1}} \\
 &= 0.000215 \text{ cm}^3 / \text{s}^2
 \end{aligned}$$

The viscosity of pure CO₂, $\mu = 0.0011817 \text{ g} / (\text{cm} \cdot \text{s})$

From equation (25), the theoretical velocity of ideal pure CO₂,

$$\begin{aligned}
 V_c &= K \frac{\mathbf{r}_c - \mathbf{r}_f}{\mathbf{m}} \\
 &= 0.000215 \text{ cm}^3 / \text{s}^2 \times \frac{2.7 \text{ g} / \text{cm}^3 - 0.9888 \text{ g} / \text{cm}^3}{0.0011817 \text{ g} / (\text{cm} \cdot \text{s})} \\
 &= 0.311 \text{ cm} / \text{s}
 \end{aligned}$$

For pure CO₂, from equation (28), shear rate is

$$\begin{aligned}
 \text{Shear Rate} &= \frac{dV_z}{dr} = V_c \left[\frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{(r_t^2 - r_c^2) + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \right] \\
 &= 0.311 \text{ cm/s} \left[\frac{-2 \times 1.5747 - (1.5875^2 - 1.5747^2) \frac{1}{1.5747 \ln(1.5747/1.5875)}}{(1.5875^2 - 1.5747^2) + \ln(1.5747/1.5875)(1.5875^2 + 1.5747^2)} + \frac{1}{1.5747 \ln(1.5747/1.5875)} \right] \frac{1}{\text{cm}} \\
 &= -9045 \text{ s}^{-1}
 \end{aligned}$$

For copolymer sample, theoretical velocity (for ideal fluid),

$$\begin{aligned}
 V_s &= V_c \times \frac{V_{co2}}{V_{sample}} \\
 &= 0.311 \text{ cm/s} \times \frac{0.004945 \text{ cm/s}}{0.471 \text{ cm/s}} \\
 &= 0.00327 \text{ cm/s}
 \end{aligned}$$

For copolymer sample, shear rate

$$\begin{aligned}
 \text{Shear Rate} &= \frac{dV_z}{dr} = Vc. \left[\frac{-2r_c - (r_t^2 - r_c^2) \frac{1}{r_c \ln(r_c/r_t)}}{(r_t^2 - r_c^2) + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)} \right] \\
 &= 0.00327 \text{ cm/s} \cdot \left[\frac{-2 \times 1.5747 - (1.5875^2 - 1.5747^2) \frac{1}{1.5747 \ln(1.5747/1.5875)}}{(1.5875^2 - 1.5747^2) + \ln(1.5747/1.5875)(1.5875^2 + 1.5747^2)} + \frac{1}{1.5747 \ln(1.5747/1.5875)} \right] \frac{1}{\text{cm}} \\
 &= -95.05 \text{ s}^{-1}
 \end{aligned}$$

APPENDIX B

NON-NEWTONIAN FLUID MODEL DEVELOPMENT

For our falling cylinder viscometer, assuming the polymer solution fit power law model, we developed the derivation of viscosity program with power law model, and get the power law model constants, m , n for our CO₂-thickener solutions. We also get the new Relative viscosity vs Shear rate figure in this new model

1 Power law model:

$$\tau = -m \left| \frac{dV_z}{dx} \right|^{n-1} \frac{dV_z}{dx} \quad (1)$$

2 Mass Balance

First, according to the total liquid volume are constant, so the liquid is displaced is equal to the liquid flowing through the annular gap.

$$-pr_c^2 V_c = 2p \int_{rc}^{rt} V_z(r) r dr \quad (2)$$

This equation can be solved with average velocity of the fluid in the annulus $\langle V_z \rangle$, and $e = 1 - k = 1 - rc/rt$.

$$V_c = \frac{2e(1-0.5e)}{(1-e)^2} \langle V_z \rangle \quad (3)$$

3 Force balance

According to Newton's 2nd Law, when terminal velocity is reached, $dv_z/dt=0$, the piston is in force balance:

$$G = F_1 + F_2 + F_3 \quad (4)$$

here, G is gravity,

$$G = \rho r_c^2 l r_c g \quad (5)$$

F_1 is the force on the piston vertical surface,

$$F_1 = 2\rho r_c l t_{r=r_c} \quad (6)$$

F_2 is the force on the piston top and bottom surface because of pressure difference,

$$F_2 = \rho r_c^2 l \frac{dP}{dZ} \quad (7)$$

F_3 is the force because of pure CO₂ buoyancy,

$$F_3 = \rho r_c^2 l r_f g \quad (8)$$

Substitute G , F_1 , F_2 , F_3 into equation (4),

$$pr_c^2 l(r_c - r_f)g = 2pr_c l t_{r=r_c} + pr_c^2 l \frac{dP}{dZ} \quad (9)$$

$$(r_c - r_f)g = \frac{dP}{dZ} + \frac{2t_{r=r_c}}{(1-e)R} \quad (10)$$

4 Momentem balance

In falling cylinder viscometer, the annular gap is so small, $r_c \rightarrow r_t$, assume the annular thin slit can be regarded as a plane slit(it introduces correction terms γ_{tc} and γ_{vc} to correct the shear stress and velocity respectively). Also, because the falling cylinder velocity is very small compared with the fluid velocity in the gap, so neglect the falling cylinder velocity(it introduces correction terms γ_{tm} and γ_{vm}). From reference[Bird, Stewart, Bigfoot, textbook, p62], for the fluid flows in the slit of 2 parallel planes,

$$t_{r=r_c} \Big|_{slit} = \frac{dP}{dZ} (0.5eR) \quad (11)$$

5 From reference(Ashare),

$$t_{r=r_c} = t_{r=r_c}^0 y_t \quad (12)$$

$$< V_z > = < V_z >^0 y_v \quad (13)$$

where, superscript 0 denotes that zeroth degree approximation. y_t and y_v are the correction for shear stress t and velocity V_z because of the assumption of plane slit and stationary falling cylinder, and $y_t = y_{tc} \times y_{tm}$, $y_v = y_{vc} \times y_{vm}$

$$y_v = 1 - e - \frac{3}{20} e^2 + \frac{1}{35} e^4 \quad (14)$$

$$y_t = \frac{1-0.5e}{1-e} \quad (15)$$

6 dP/dZ ,

From equation 10, 11, and 12, we can get dP/dZ

$$\frac{dP}{dZ} = \frac{(r_c - r_f)g}{1 + \frac{e}{1-e} y_t} \quad (16)$$

7 Power law fluid

From reference (Fredrickson and Bird, Ind. Eng. Chem., 50, 347(1958)), the average velocity of the fluid in the plane slit,

$$\langle V_z \rangle_{slit} = \left(\frac{\Delta p e R}{2 m L} \right)^s \frac{e R}{2(s+2)} \quad (17)$$

where, $s=1/n$

8 Final equation

Combine equation(3, 13, 16, 17), we can get:

$$V_c = \frac{2e(1-0.5e)}{(1-e)^2} \cdot \frac{eR}{2(S+2)} \cdot \left(\frac{eR}{2m} \right)^s \cdot y_v \cdot \left[\frac{(r_c - r_f)g}{1 + \frac{e}{1-e} y_t} \right]^s \quad (18)$$

9 Model constants

In reference[Ashare], they did experiment with different cylinder(different cylinder density ρ_c , the same size), so, the same e , it is easy to get constant s , if one log both sides of the

final equation, get straight line of $\log V_c$ vs. $\text{Log} \left[\frac{(r_c - r_f)g}{1 + \frac{e}{1-e} y_t} \right]$, and the sloap is the s , then

substitued a pair of data(V_c , ρ_c), can get constant m .

While in our experiment set, our cylinders are the different size(rc), so different e , with the same density ρ_c , the method is not valid here. So we try to get constant s , m with minimum difference between calculated velocity and experimental velocity.

$$\Sigma[(V_{cal} - V_{exp})^2] = \min$$

In equation 18, we write a program, with two loops, iterate m from 0.001 to 0.3, corresponding to 1 to 300 times viscosity improvement if the fluid is Newtonian fluid, and iterate s from 1 to 3, we get s , m for the different copolymer solutions.

APPENDIX C

C++ PROGRAM FOR POW-LAW MODEL

```
//This program is for getting power law parameters (m, s=1/n), from poly fluoroacrylate styrene
// copolymer viscosity results with the falling cylinder viscometer.
// The program can be run in Borland C++ environment without any problem
// In Unix and Visual C++ environment, need a little modification.

#include <iostream>

#include <math.h>

#include <fstream.h>

#include <conio.h>

int main(){

    ofstream fresult("result.txt");

    fresult<<"RESULT for copolymer solution"<<endl;

    fresult<<" s          m          delv%"<<endl;

    double m;    //power law parameter

    double s;    //power law parameter

    double minimum=0.1; // initial lowest difference, E(vcal-vexp)^2
```

```

//terminal velocity(cm/s) for falling cylinder in (29%FA) soln.

//double vcexp[]={0.0023, 0.00388, 0.02536, 0.118,
//      0.004104, 0.004945, 0.015};

//double vcexp[]={0.00479, 0.01356, 0.05091, 0.33};      //3wt%

//double vcexp[]={0.03022, 0.03597, 0.1957,
//      0.84, 0.01325, 0.1334, 0.35};      //1wt%

//double vcexp[]={0.04997, 0.174, 0.093,
//      0.362, 1.08};      //0.2wt%

double vcexp[]={0.06, 0.15};      //0.1wt%


double vccal[2]; //calcuated falling cylinder velocity(cm/s)


//falling cylinder diameter(inch)

//double rc[]={1.2438, 1.2428, 1.2399, 1.2311,
//      1.2438, 1.2399, 1.2339};      //5wt%

//double rc[]={1.2438, 1.2428, 1.2399, 1.2311}; //3wt%

//double rc[]={1.2438, 1.2428, 1.2399, 1.2311,
//      1.2438, 1.2399, 1.2339};      //1wt%

//double rc[]={1.245, 1.2428, 1.2438,
//      1.2399, 1.2339};      //0.2wt%

double rc[]={1.245, 1.2428};      //0.1wt%


double rt=1.25;      //tube diameter(inch)

```

```

double R=rt*2.54/2; //tube radius (cm)

double deltapg=(2.7-0.9888)*980;    //(p0-p)*g, p(density)

for (m=0.001; m<0.3; m+=0.001){

    for (s=1; s<3.0; s+=0.01){

        double sum=0;

        for (int i=0; i<2; i++){ // for different cylinder

            double e=1-rc[i]/rt;

            double phiv=1-e-3/20*e*e;

            double phit=(1-0.5*e)/(1-e);

            //cout<<"e:"<<e<<"  phiv"<<phiv<<"  phit:"<<phit

            //<<"  s:"<<s<<"  m:"<<m<<"deltapg:"<<deltapg<<endl;

            vccal[i]=2*e*(1-0.5*e)/(1-e)/(1-e)*e*R/2/(s+2)

                *exp(s*log(e*R/2/m*deltapg/(1+e/(1-e)*phit)))

                *phiv;

            // cout<<"debug:"<<endl;

            //cout<<"vccal["<<i<<"]:"<<vccal[i]<<endl;

            fresult<<s<<"          "<<m<<"          "

                <<((vccal[i]-vcexp[i])*100)<<endl;

            sum+=(vccal[i]-vcexp[i])*(vccal[i]-vcexp[i]);

        }

        fresult<<"                               Sum: "<<sum<<endl;

    }

    if(sum<minimum) {

        minimum= sum;
    }
}

```

```
    cout<<"m: "<<m<<"s: "<<s<<" Sum: "<<sum<<endl;

    }

    }//end of for(s)

    }//end of for(m)

    cout<<"It is done!";

    getch();

    return 0;

}
```

APPENDIX D

MATLAB PROGRAM FOR FALLING CYLINDER VISCOMETER CALIBRATION

```
% The following is the matlab program, used for falling cylinder viscometer calibration.

% the function is for get Vct of different piston,

% also the dvzdr close to the piston

% input the piston diameter(inch), co2 density(g/cm3), co2 viscosity(g/cm/s)

function vct=dvzdr3(piston,density,viscosity)

rc0=piston*2.54/2.0; %change to cm, radius

rt=1.250*2.54/2.0; %change to cm, radius

pf=density; % density of co2

pc=2.7; %density of aluminum piston

pc_pf=pc-pf; %density difference

g=980; %gravity constant

dr=(rt-rc0)/20;

rt0=rc0+(rt-rc0)/20*19;

rc=rc0:dr:rt0;

dvzdr=zeros(20); %initiate dvzdr[21]

for l=1:20

    gap(l)=rt-rc(l);
```



```

dem0(l)=log(rc(l)/rt)*(rt^2+rc(l)^2)+(rt^2-rc(l)^2); % common term in downstairs
j1(l)=-4/(log(rc(l)/rt)*(rt^2+rc(l)^2)+(rt^2-rc(l)^2)); % one term in K
k1(l)=(-2*rc(l)-(rt^2-rc(l)^2)/rc(l)/log(rc(l)/rt))/(log(rc(l)/rt)*(rt^2+rc(l)^2)+(rt^2-
rc(l)^2))+1/rc(l)/log(rc(l)/rt);
k(l)=rc(l)*g/(rc(l)*j1(l)-2*k1(l)); % get K
vct(l)=k(l)*pc_pf/viscosity; % terminal velocity

r(l)=rc(l); % calculate the point close to piston
dvzdrc(l)=vct(l)*((-2*r(l)-1/r(l)/log(rc(l)/rt)*(rt^2-rc(l)^2))/(rt^2-
rc(l)^2+log(rc(l)/rt)*(rt^2+rc(l)^2))+1/r(l)/log(rc(l)/rt));
end %get dvzdr

% rinch=r*2/2.54 %return to inch unit

gapmin=gap+0.00015*2.54
gapmax=gap-0.00015*2.54
vct % show terminal velocity cm/s
dvzdrc % show dvzdr close to the piston

plot(gap,dvzdrc)
title('shear rate vs gap');
xlabel('gap (cm)');
ylabel('dvz/dr (s-1)');

```

```

deltagap1=[0.0031,0.0031,0.0031];
deltavct1=[0.198,0.188,0.183];
deltagap2=[0.00295,0.0031,0.00325];
deltavct2=[0.188,0.188,0.188];
deltagap3=[0.00505,0.00505,0.00505];
deltavct3=[0.641,0.568,0.543];
deltagap4=[0.0049,0.00505,0.0052];
deltavct4=[0.568,0.568,0.568];
deltagap5=[0.00805,0.00805,0.00805];
deltavct5=[1.41,1.3,1.02];
deltagap6=[0.0079,0.00805,0.0082];
deltavct6=[1.3,1.3,1.3];

deltagap1=deltagap1*2.54;
deltagap2=deltagap1*2.54;
deltagap3=deltagap1*2.54;
deltagap4=deltagap1*2.54;
deltagap5=deltagap1*2.54;
deltagap6=deltagap1*2.54;

deltagap=[0.0031,0.0031,0.0031,0.00325,0.0031,0.00295,0.00505,0.00505,0.00505,0.0052,
0.00505,0.0049,0.00805,0.00805,0.00805,0.00820,0.00805,0.0079];

```

```

deltavct=[0.198,0.188,0.183,0.188,0.188,0.188,0.641,0.568,0.543,0.568,0.568,0.568,1.41,1.3,
1.02,1.3,1.3,1.3];
deltagap=deltagap*2.54;

plot(gap,vct,gapmax,vct,gapmin,vct,deltagap,deltavct,'*')
title('ideal terminal velocity of different piston');
xlabel('gap (cm)');
ylabel('Vct (cm/s)');

```

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